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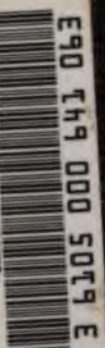
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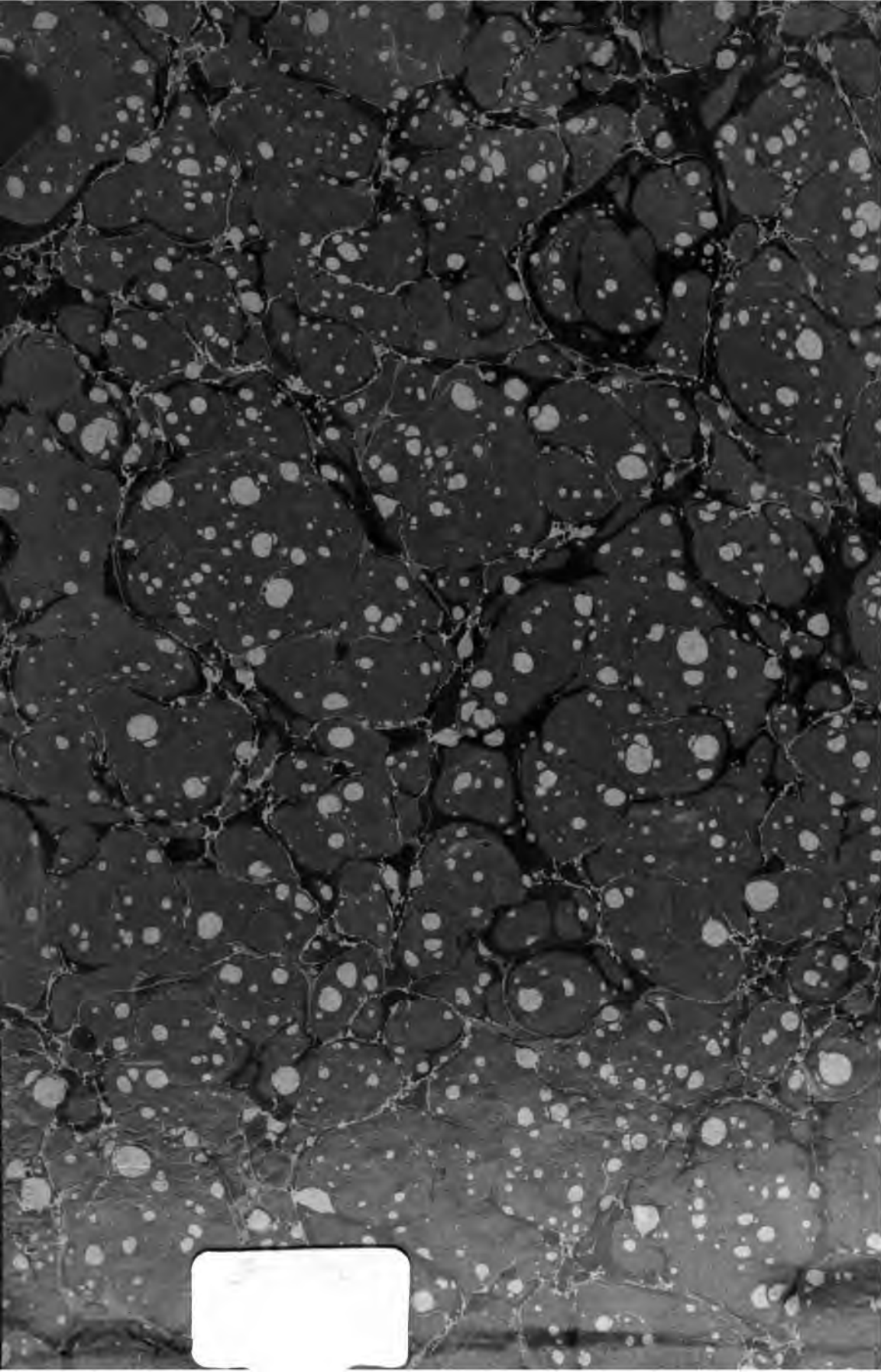
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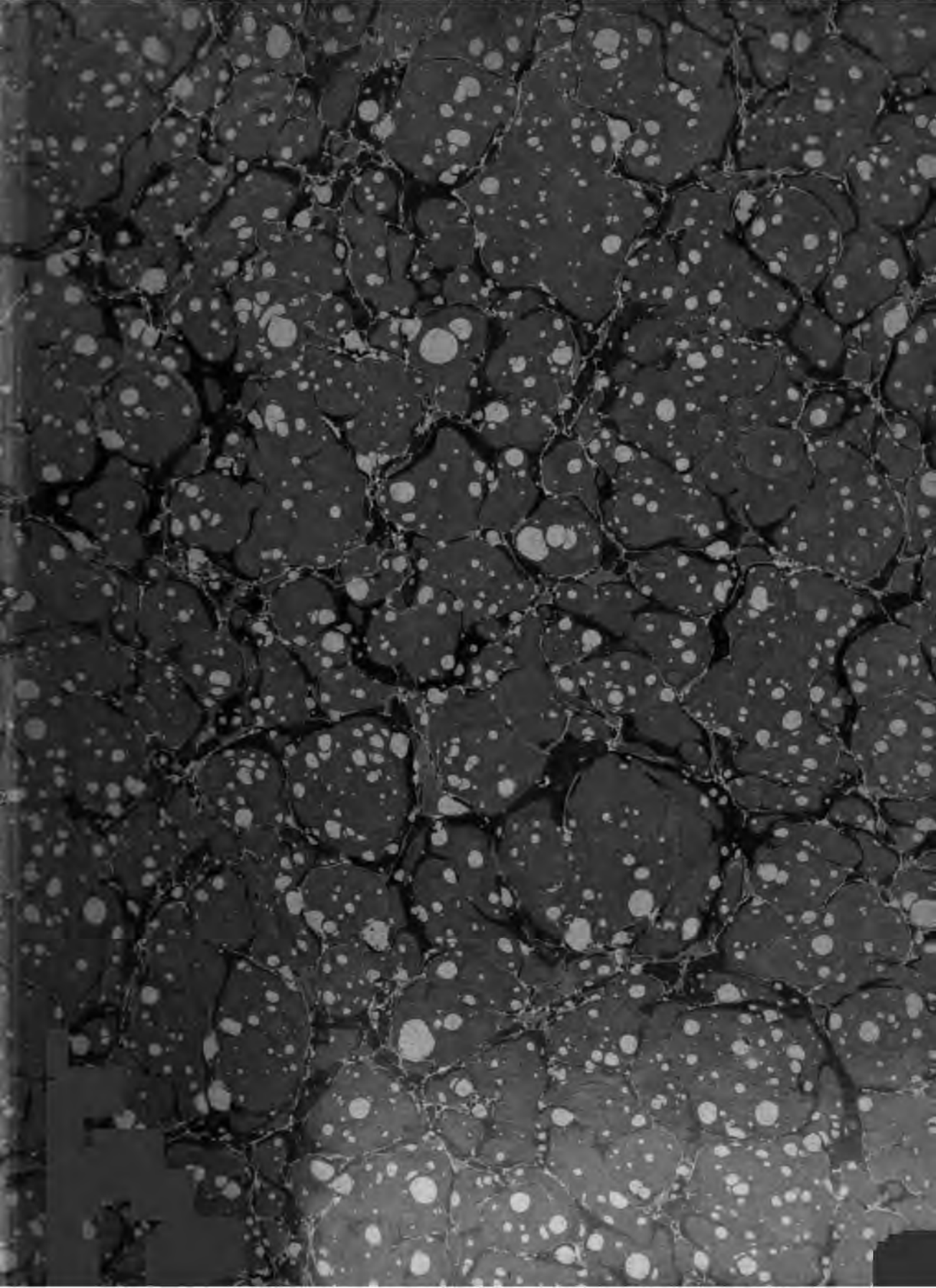
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THE
PHYSICAL REVIEW

*A JOURNAL OF EXPERIMENTAL AND
THEORETICAL PHYSICS*

CONDUCTED WITH THE CO-OPERATION
OF THE

AMERICAN PHYSICAL SOCIETY

BY

EDWARD L. NICHOLS, ERNEST MERRITT,
AND FREDERICK BEDELL

VOL. XXV

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THE
PHYSICAL REVIEW.

THE MELTING POINTS OF RHODIUM AND IRIDIUM,
AND THE USE OF THE NERNST GLOWER IN
HIGH TEMPERATURE MEASUREMENTS.

BY C. E. MENDENHALL AND L. R. INGERSOLL.

IN the following paper we shall consider the use of the Nernst glower for the optical measurement of certain high temperatures, and discuss the result of our determinations, by this method, of the melting points of rhodium and iridium, and the temperature of normal brilliancy of the glower, as well as the melting point of its material and its radiation constants.

As is well known there are two general radiation methods which have proved satisfactory for temperature measurements — one based on the variation of total radiation with temperature, *i. e.*, $J = \sigma T^4$; the other on the variation with temperature of the emission of a small group of wave-lengths, that is on the isochromatic radiation curve, $\log E_\lambda = K_1 + K_2/T$. As usually used they are based on the theory and radiation laws of a "black body" and can only be correctly applied to determine the temperature of such a body. In the case of non-black bodies such as the Nernst glower since there is no theoretical basis for any radiation law the measurement of high temperatures, even more than in the case of black bodies, depends on the extrapolation of an empirical law. The method of isochromatic observations at some wave-length of the visible spectrum is much simpler to carry out than the total radiation one, and also various considerations (see *sources of error*) indicate that the isochromatic radiation formula is the safest to extrapolate. Our work, therefore,

depending as it does on the determination of the various temperatures of the Nernst glower, is based on the extrapolation of the isochromatic

$$\log E_{\lambda} = K_1 + K_2/T$$

where E_{λ} is the emission of the radiation of wave-length λ at the absolute temperature T , and K_1 and K_2 are constants. To establish a temperature scale on this basis evidently requires observations of the values of E_{λ} — measured in any units whatever — at only two known temperatures, for which purpose we use the melting points of gold and platinum. Knowing this, the temperature corresponding to any other emission may be very easily computed. Substantially the same method has been applied by Waidner and Burgess¹ to the platinum strip of a Joly melder.

ARRANGEMENT OF APPARATUS.

The arrangement of apparatus is shown in Fig. 1. The glower

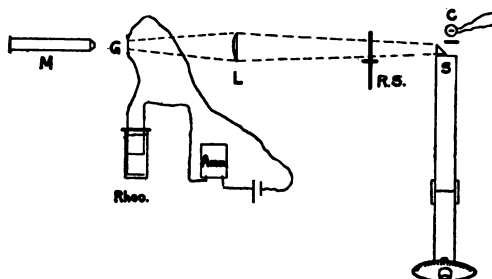


Fig. 1.

G was of the ordinary 110 volt D.C. type furnished by the Nernst Lamp Company of Pittsburgh, and was used with 200 and sometimes even with 500 volts and a large ballast resistance, for in this way only could it be run steadily at the lower temperatures. A millimeter and continuously variable resistance (electrolytic) made possible its perfect control. It was mounted with possibility of adjustment and placed so that it might be observed with the microscope M from one side, while from the other an image was thrown by the lens L on the slit S of a Martens-König spectrophotometer. The aperture of the lens and size of image were so chosen as always

¹Waidner and Burgess, Bull. Bureau of Standards, 1, p. 189, 1904.

to much more than cover the slit, and more than fill the aperture of the collimating lens of the spectrophotometer. This being so, the brightness of the corresponding half-field in the spectrophotometer was independent of small changes in the position of the glower.

As the comparison source *C*, a 2 c.p. incandescent lamp behind a ground glass screen was used, the current through it being maintained constant. To increase the accuracy of reading at the higher temperatures, where the ratio of the intensity of the glower to that of the comparison source became large, a rotating sector *RS* was introduced between the lens and the slit. The sectors were made to reduce approximately in the ratios 1/5, 1/10, and 1/25, the exact values being determined by measurements with a circular dividing engine. The glower was usually protected by a metal shield and cover, to increase the constancy and uniformity of its temperature.

METHOD OF OBSERVATION.

The method of observation was in brief to place on top of the glower a very minute particle of the metal to be tested, gradually increase the glower current until the melting point was reached, and then make a number of settings of the spectrophotometer at that temperature, the wave-length used in almost all cases being $\lambda = .606 \mu$. In some cases, notably gold and platinum, the observer at the microscope could so control the glower current as to maintain the globule of metal part melted and part solid, for some time, during which spectrophotometer settings could be made. In other cases it was found better to determine the current corresponding to the melting temperature by a number of trials, and then to maintain this steady current while the photometer was being read. In cases where it was impossible to maintain this half-melted half-solid condition, it was the melting point and not the point of solidification which was taken, as the latter is subject, in small particles, to great effects of undercooling. It was also the practice not to take the "first melt" of the particles, but subsequent meltings after the globule was in good contact with the glower surface. In practically all cases standardizing observations were made with each glower upon the melting points of gold and platinum, though, as can be seen from Table I. and Fig. 2, the slope of the isochromatic

—determined by $\log E_{\text{platinum}} - \log E_{\text{gold}}$ — was remarkably constant for all glowers; that is, K_2 varied but little for the different glowers. The measurement in this way of the emission of the glower in terms of a constant comparison lamp was all that was necessary to determine the temperature scale; and the observations were best handled graphically by simply plotting $\log E_{\text{gold}}$ against $\frac{1}{T_g + 273}$, and $\log E_{\text{platinum}}$ against $\frac{1}{T_p + 273}$ where E_{gold} and E_{platinum} are the glower emissions in terms of the comparison lamp. The reciprocal of the temperature corresponding to any other emission E could then be read off at once from the straight line connecting the standard points.

STANDARDIZING TEMPERATURES.

The melting point of gold was taken at 1065°C. which is probably correct to about a degree. The melting point of platinum is however still quite uncertain, and as practically all very high temperature measurements are based in some way on the melting point of platinum, all such temperature determinations above say 1400°C. are subject to corrections of from 10° to over 100° , depending on the value accepted for platinum. The observations of Waidner and Burgess,¹ and of Nernst and v. Wartenburg² place the platinum melting point at about 1745°C. , while Holborn and Valentiner³ in their recent work put in at 1789°C. It being at present impossible to decide finally between these two, we give in our tables of results two values for all the temperatures determined, calculated on the respective bases of 1745°C. and 1789°C. for the platinum melting point.

SOURCES OF ERROR.

1. *The Use of Paschen's Isochromatic Equation.*— Since nearly all our measurements involve an extrapolation, it is important to consider carefully the choice of the radiation function which is to be extrapolated.

The work of Paschen⁴ shows that up to temperatures of about

¹ Waidner and Burgess, Paper before Am. Phys. Soc., Feb., 1907.

² Nernst and v. Wartenburg, Verh. d. Deutsch. Phys. Ges., 1906, pp. 48 and 146.

³ Holborn and Valentiner, Ann. d. Phys., 22, p. 1, 1907.

⁴ F. Paschen, Wied. Ann., 58, p. 455, 1896; 60, p. 662, 1897.

1400° C., or as far as he could test it, and for wave-lengths such that $\lambda T < 3,000$, an equation of the form of Wien's

$$E_{(\lambda, T)} = C_1 \lambda^{-a} e^{-c/\lambda T} \quad (1)$$

represents with very considerable accuracy the form of the energy curve for various kinds of radiating surfaces; that the isochromatic radiation is well represented by

$$\log E_{(\lambda, T)} = K_1 + K_2/T \quad (2)$$

and that the total radiation from these surfaces follows quite closely the law

$$J = \sigma T^{a-1} \quad (3)$$

where $a > 6$ ($a = 5$ for a black body). As they have no theoretical basis except for a black body, and as such measurements as we are concerned with involve very considerable extrapolations beyond the range of experimental test, it is well to consider briefly the probable validity of these empirical laws. Since the total radiation of a non-black body can only approach as a limit that of a black body, law (3) cannot be expected to hold indefinitely with a constant $a > 5$; a must then diminish towards 5 for high temperatures, and the greater the initial value of a , the greater the final change. Equation (2) is of course a necessary consequence of (1), but (2) *might* be true and (1) not; (3) is a necessary consequence of (1), and if (3) does not hold with constant a , (1) cannot. But a might vary considerably (enough to reconcile (3) with the facts) and still give an approximately linear isochromatic, for (1) may be written

$$\log E_{(\lambda, T)} = \log C_1 - a \log \lambda - \frac{C_2}{\lambda T} \log e$$

which would, for values of λ near unity (1μ), — since C_1 has been found to be for those radiating surfaces so far studied, between 500,000 and 2,000,000,¹ give an isochromatic almost linear in $\log E$ and $1/T$, even although a varied with T .²

¹ F. Paschen, loc. cit.

² In this connection we have made some attempts to measure a for the glow to see if it is a noticeable function of the temperature. These will be referred to later.

Equations (1) and (2) have recently been discussed by Burgess in a somewhat different manner in connection with the observations of Waidner and Burgess on the radiation of a platinum strip; and these observations also confirm the validity of the linear isochromatic equation (2).

It seems to us then, from these considerations, that the isochromatic radiation formula is, for non-black bodies, the safest to use in extrapolating for high temperature measurements. Two indications of the general correctness of this conclusion are furnished by the results. One is given by the determination of the melting point of palladium which was found to be at 1548° C. or 1576° C. according as the melting point of platinum is assumed at 1745° C. or at 1789° C. Nernst and v. Wartenburg¹ who found the lower value for platinum placed palladium at 1541° C., while Holborn and Valentiner² set it at 1582° C., on the other basis for platinum. It will be noted that our values are as much above one as below the other; and while not furnishing in itself a justification for *extrapolating* the isochromatic radiation formula, this does show that it is sensibly a straight line at least between the gold and platinum points. The other point in support of our method depends on measurements made with two different wave-lengths, viz., $\lambda = .606 \mu$ and $\lambda = .493 \mu$. The following table shows that temperatures measured with the two different wave-lengths check to within the probable error of measurement, and this could not be expected to be the case unless our equations are at least approximately correct.

Platinum melting point taken at 1789° C.

Glowers No. 23, melting point of rhodium	$\lambda = .493 \mu$	$T = 1967^{\circ}$ C.
	$\lambda = .606 \mu$	$T = 1970^{\circ}$ C.

Glowers No. 24, temperature of normal brilliancy	$\lambda = .493 \mu$	$T = 2189^{\circ}$ C.
	$\lambda = .606 \mu$	$T = 2198^{\circ}$ C.

2. *Temperature Difference Between the Globule of Metal and the Glower.* — This is dependent on the size of the particle and its contact with the glower and may give rise to an uncertainty, due to the use of too large a piece of metal, or of poor contact with the glower, of as much as 100 degrees or more unless proper precautions are

¹Nernst and v. Wartenburg, loc. cit.

²Holborn and Valentiner, loc. cit.

taken. For example, if a small rider of platinum foil only .007 inch thick is hung on the glower, its apparent melting point may be as much as 200 degrees too high, and even a very small piece of metal when first put on the glower and in poor contact, may require a glower temperature of perhaps 50 degrees or more above its melting point before it will melt. This source of error was studied by using globules of various sizes, and guarded against by taking observations only on globules so small (.05 mm.) that the

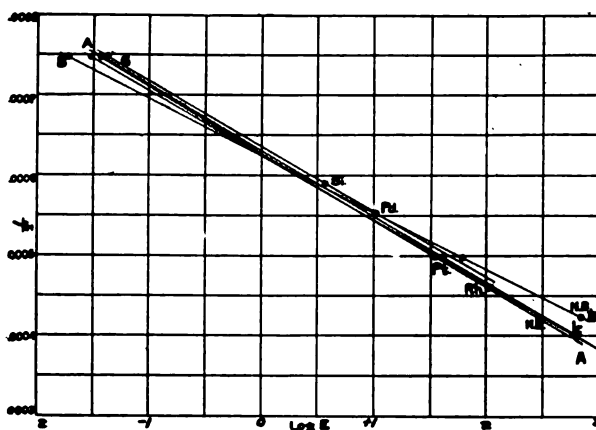


Fig. 2.

melting point was observed to be practically independent of the size. Furthermore the method of measurement tended to eliminate the effect of any small outstanding difference of temperature still remaining; for about the same sized globules of the various metals, gold, platinum, rhodium, iridium, etc., were used, and if this difference can be supposed roughly proportional to the temperature it can be easily seen that it can have little or no effect on the determination of the melting point.

3. *Alloying of the Metals.* — The results are given only for those metals which draw into a clear metallic bead on the surface of the glower: the consistency of readings for successive melts, and for old and fresh globules, renders any appreciable contamination by the material of the glower very improbable. Only in rare instances, and then only when the glower had been used with various metals,

TABLE I.—Continued.
Melting Points and Temperatures of the Nernst Glower in Degrees C.

Glower No.	2	3	4	5	6	7	8	9	18	22	23	24	34	35	37	38	39	40	41	Mean.
Temp. of Normal Brill. of Glower.		2113		2127			2154		2074	1934	2158	2117								2124
Remarks.		2194 with shield		2203 with shield			2234 with shield		2154 no shield	1997 large glower shield	2240 no shield	2198 no shield								2204
Melting point of Glower Material.							2363											2393		
Log $E_{\text{plat.}}$ —log E_{gold}					3.070		2473				2.954	3.023					3.085	2500	3.013	
C_1					17000				* Second value is obtained	*	{ 16350	{ 16700					17100		16700	16800
					16300				by using $\lambda = .493$	*	{ 15700	{ 16100					1640		16000	16200

TABLE II.

Summary of the Principal Determinations of the Following Points.

Substance.	Melting Point. °C.	Method.	Melting Point Accepted for Platinum. °C.	Observer.
Silicon.	1430	Optical.	1745	Tone.
	1434 } ± 8		1789	M. and I.
	1452 } ± 8		1789	"
Palladium.	1541	Wanner pyrometer.	1745	Nernst and v. Wartenburg.
	1582	Thermoelectric.	1789	Holborn and Valentiner.
	1548 } ± 5	Optical.	1745	M. and I.
	1576 } ± 5	"	1789	"
	1576 } ± 5	"	1789	"
Rhodium.	1907 } ± 5	"	1745	"
	1968 } ± 5	"	1789	"
Iridium.	2200-2300	"	1745	Weyde (1879).
	1950			Violle (1879).
	2292 } ± 10			M. and I.
	2388 } ± 10			"
Temperature of glower at normal brilliancy.	2200-2450 abs. ¹	Max. of energy curve.	1745	Lummer and Pringsheim.
	2360 abs. ¹	Efficiency.	1745	Ingersoll.
	1800 abs.	Thermoelectric.	1745	Hartman.
	2400 abs.	Optical.	1745	M. and I.
	2480 abs.	"	1789	"
Melting point of magnesium oxid.	1910	Wanner pyrometer.	1745	Goodwin and Mailey.
	1980-2023	Optical.		M. and I.
Melting point of glower material.	2380	"	1745	"

have inconsistencies arisen which would call for alloying as an explanation. Globules of different metals on the same glower are of course kept as far apart as possible.

4. *Oxidation.* — Observations have been made only in air so far, and only on those metals which oxidize little if at all. Oxidation can usually be readily detected with the microscope.

¹ These values were based on the old values of the black body radiation constants, which have subsequently given by extrapolation the value of 1745 for the platinum melting point.

5. *Purity of the Metals.*—For standardizing points, Heræus platinum and some pure gold kindly given us by Professor L. Kahlenberg, were used. The palladium also came from him. Many specimens of rhodium, ruthenium and iridium were tried, for most of which we are indebted to Professor V. Lenher: they were all, so far as could be learned, prepared by Schuchardt, but no self-consistent results could be obtained with them. That is to say, different samples of supposedly the same metal gave widely different melting points, and different particles of even the same sample would vary considerably. Finally some specimens of iridium, rhodium and ruthenium were obtained from W. C. Heræus, which were furnished as pure, save that the iridium might contain traces of ruthenium. These gave very uniform and consistent readings, and the results here given refer entirely to these specimens. Observations with ruthenium have been so far unsatisfactory on account of its tendency to flux with the glower, in which respect it differs entirely from iridium and rhodium.

DISCUSSION OF RESULTS.

The results of our observations are summarized in Tables I. and II. and may be discussed under separate heads, in the order of ascending temperatures. As metals to be studied we have chosen those for whose melting points little if any data could be found, limited by the fact that a number of such metals either oxidize or flux with the material of the glower at the melting temperature. Some of these may be studied by a modified method later.

1. The melting point of silicon, 1434° C. or 1452° C. (according to the value accepted for platinum). It is very easy to observe because of marked surface changes on solidification but the separate determinations show rather large variations. One of the samples used was furnished by Mr. Watts, of the electrochemical department, and supposed to be 99 per cent. pure. Tone,¹ working with silicon which analysis showed to be 95.3 per cent. pure, found the melting point at 1430° C.

2. The melting point of palladium, 1548° C. or 1576° C. was determined as a check on the method. As already noted these values form practically a mean of the best previous determinations.

¹ T. J. Tone, Trans. Am. Electrochem. Soc., 7, p. 245, 1905.

3. The melting point of rhodium, 1907°C . or 1968°C . is such a sharp and easily determined point that it should prove useful as a reference point in high temperature measurements.

4. Temperature of normal brilliancy of the glower. For an .8 amp. 110 volt glower 1.04 mm. in diameter, this may be perhaps placed at 2120°C . or 2200°C ., and for one 1.30 mm. in diameter, some 200 degrees lower. This is of course not a very definite point, but is of interest, partly on account of its bearing on the question of luminous efficiency, and partly in connection with recent discrepant estimates of the "temperature of the glower." Determinations have been made by (a) Lummer and Pringsheim¹ from measurements of the wave-length of maximum energy, applying Wien's law and assuming that the glower had radiating properties between those of a black body and platinum; they give the limits 2200° and 2450° absolute: (b) by one of us,² from measurements of the luminous efficiency of the glower, assuming that it is a black body; this gives 2360° absolute: (c) by Hartman,³ using thermocouples of various sizes and an extrapolation method of E. L. Nichols⁴ to eliminate the effect of conduction of the wires. He concludes that the temperature is only about 1800° absolute.

The first two of the above agree fairly well with our present determinations, which may be stated in round numbers at 2400° to 2475° absolute for the smaller size of glower now in general use. Unfortunately, without making efficiency measurements and temperature measurements on the same glower and under the same conditions of current and voltage, it is impossible to draw any definite conclusions as to the presence of selective emission which would make the glower more efficient at a given temperature than a black body. However the fair agreement of our determinations with that of Ingersoll indicates that such selective emission, if present at all, is small.

That Hartman's result of less than 1600°C . is widely in error can be readily shown by putting a small bit of platinum on the glower and noting that it melts at a temperature far below that of

¹ Lummer and Pringsheim, *Verh. phys. Ges. Berlin*, 1, p. 215, 1899.

² L. R. Ingersoll, *PHYS. REV.*, 17, p. 371, 1903.

³ L. W. Hartman, *PHYS. REV.*, 22, p. 351, 1906.

⁴ E. L. Nichols, *PHYS. REV.*, 10, p. 234, 1900.

normal brilliancy. But if it is in the form of a fine wire or strip hung over the glower so that part of it is comparatively cool, it cannot be melted at all, or at least only with the greatest difficulty. Herein probably lies the explanation of Hartman's low results, for it would seem that Nichol's extrapolation method does not by any means compensate for the cooling effect of the leads, at least where poor thermal conductivity of the heated body and high temperatures are concerned, so that great temperature gradients are possible. In support of this idea may be mentioned results obtained by this method on the temperature of the candle flame.¹ They place it at less than 1675°C. , while it is well known that a fine Wollaston wire may be readily melted in it. To remove the objection that the Wollaston wire may be an alloy of platinum, we used Heræus platinum foil and found that very fine strips could be fused in almost any part of the flame.

5. Melting point of iridium, 2292°C. or 2388°C. To obtain this temperature easily it was desirable to keep the ends of the glower from becoming overheated by hanging strips of platinum on them. Under these circumstances the iridium could be melted into a globule and this remelted some two or three times before it had entirely sublimed. A glower current of 1.3 to 1.5 amp. was required and a $1/25$ sector was introduced, as the radiation at the wave-length used was roughly 20,000 times greater at this temperature than at the gold melting point.

6. Melting point of the material of the glower, about 2380°C. or 2490°C. This had to be obtained by slowly raising the temperature of the glower, keeping the photometer set for balance, until fusing occurred, which would be at perhaps 1.8 amp. The values are only an indication, probably too low if anything, of the maximum temperatures attainable with glowers of ordinary composition; by using pure zirconium oxide the limit could probably be raised somewhat. In this connection we have determined roughly the melting points of several specimens of "C.P." magnesium oxide—one from Schuchardt, one from Eimer and Amend, and one furnished us by Mr. Watts. The melting points range from 1980° to 2023°C. (Pt at 1745°), somewhat higher than that ob-

¹ E. L. Nichols, *loc. cit.*, p. 248.

tained by Goodwin and Mailey,¹ viz., 1910° C. It is of interest to note that both these figures are far below the usual estimate, based on experience, of those who have used magnesium oxide practically.

CHANGES OF RADIATING POWER OF THE METALS AT THE MELTING POINT.

There are a number of very interesting phenomena exhibited by small metallic particles on a Nernst glower, some of which we believe to have escaped notice heretofore — as for instance, the translation, or “walking” of certain particles of metal from one end of the glower to the other. These will be described at length in a forthcoming paper, but it will not be out of place to mention here the surface changes which occur in the metals studied, at their melting points. Thus a surface change so slight as possibly to escape notice in the ordinary process of observing the melting point could be readily detected as a change in the relative brightness of the globule and the glower. Gold shows a marked increase of radiating power on melting; palladium, platinum, rhodium and iridium show the same to a smaller extent, while silicon shows the reverse effect very markedly. With rhodium a second change was also observed at about 1100° C. consisting of a very marked increase of radiating power as the temperature fell — the reverse of the effect at the melt-point — a slight rise in temperature being sufficient to reverse the effect.

THE RADIATION CONSTANTS OF THE NERNST GLOWER MATERIAL.

If we assume that a law of the form of Wien's applies to the glower, we can interpret the slope constant of the isochromatic as $K_2 = \log e \cdot \frac{C_2}{\lambda}$, from which C_2 can be determined. This gives as a mean value $C_2 = 16,500$, which by comparison with the values for a black body and for polished platinum indicates that the glower material is less black even than platinum, as far as visible radiations are concerned.

If we furthermore suppose that a law of the form of Stefan's $J = \sigma T^{\alpha-1}$ holds, it is of interest to determine α , especially to see

¹ Goodwin and Mailey, Trans. Am. Electrochem. Soc., 9, p. 93, 1905.

whether it is a function of T . This we have attempted to do in two ways, but with unsatisfactory results. First, by comparing the monochromatic intensity of radiation of the glower with that of platinum for two known wave-lengths, and at several known temperatures. Such a comparison gives at each temperature a value of α in terms of α for platinum — but it is quite indirect. Second, by measuring the total intensity of radiation of the glower at various temperatures. The results can only be considered to give as a first approximation a value for α of about 9 — higher than for any radiator studied before. They gave no consistent evidence of a variation of α with T .

SUMMARY.

By a graphical extrapolation of the empirical isochromatic radiation formula we have determined the working temperature, and also the maximum attainable temperature of the Nernst glower and obtained at least approximate values for two of its radiation "constants." The glower has also been used as a species of optical meldometer, which, for the determination of high temperature melting points, seems to have certain decided advantages, namely, simplicity of method, great temperature range available, and, at least for certain classes of metals, freedom from contamination and alloying of the metals used. We have applied this method to the determination of a number of melting points, most important of which are those of rhodium at 1907° C. or 1968° C. according to the value accepted for the platinum melting point, and iridium at 2292° C. or 2388° C.

PHYSICAL LABORATORY,
UNIVERSITY OF WISCONSIN,
April, 1907.

MERCUROUS SULPHATE, CADMIUM SULPHATE AND THE CADMIUM CELL.

By G. A. HULETT.

THE previous work¹ on standard cells developed a number of facts which indicated that there was some interaction between the cadmium sulphate solution and the mercurous sulphate of the depolarizer, and now considerable experimental evidence on this question has been obtained. From the standpoint of the electrolytic dissociation theory we might expect mercurous sulphate to be less soluble in a cadmium sulphate solution than in water, since the two salts have a common ion. But the solubility was found to be about five times as great in a saturated cadmium sulphate solution as it was in water, and this fact suggested that the common ion might be ineffective in preventing hydrolysis of the mercurous sulphate. The solubility determinations indicated the presence of about a gram of mercury in a liter of the saturated solution but the solubility varied with the time the system had been rotated. This mercurous sulphate, which had been rotated with the cadmium sulphate solution and mercury, gave abnormal results when used as the depolarizer of cells. The attempt to form mercurous sulphate directly in the cadmium sulphate solution by the electrolytic method also gave an abnormal product. These results were only to be understood after more information had been gained about the conditions of equilibrium of the system (mercurous sulphate, mercury, cadmium sulphate and solution). Accordingly an apparatus was devised by which it was possible to rotate this system at a constant temperature and at any desired speed. By means of an adjustable anode of cadmium amalgam, cadmium sulphate and solution, it was possible to determine any change in the E.M.F. between the mercury and the solution of the rotated system, and thus it was possible to follow the changes of concentration of mercury in the solution.

¹Zeit. Phys. Chem., 49, 483, 1904. PHYS. REV., 22, 321 (and 23, 166).

On rotating the cathode system of the cadmium cell, it was found that the E.M.F. increased steadily for over two weeks and was only fairly constant on continued rotation. The experiment was repeated three times with fresh materials and, while the results varied somewhat, the maximum increase was about .00140 V. After the system had been rotated for thirty days it was allowed to rest but the E.M.F. did not remain constant, it decreased 0.00007 V. the first six hours, 0.00013 in twenty-four hours and then more slowly as time passed. The system was therefore not in equilibrium.

The mercurous sulphate from this rotated system was used as the depolarizer of two cadmium cells. For cell A49 the mercurous sulphate was first brought into a Gooch crucible and washed with a little fresh cadmium sulphate solution, while for cell A50 the depolarizer direct from the rotated tube was used. These cells were set up June 11, 1906, and have since been maintained at 25°. The basis of all E.M.F. values given in this article are Clark cells with electrolytic mercurous sulphate as depolarizer. Their value as determined by absolute measurements is 1.42040 V. at 25°.

Cell.	June 12.	June 14.	June 17.	June 23.	June 26.	July 7.
A49	1.01863	1.01875	1.01868	1.01856	1.01855	1.01847
A50	64	64	64	60	55	47

Cell.	August 14.	October 22.	December 19.	January 3.	February 26.
A49	1.01839	1.01827	1.01823	1.01817	1.01814
A50	38	29	26	20	15

The high preliminary value of these cells and the subsequent decrease is characteristic of cells which contain basic mercurous sulphate in the depolarizer. The cells showed no tendency to stop at the normal value, 1.01840. The results show that the rotated system did not come to equilibrium even when rotated at constant temperature for a month, and unless the changes were due to the dissolved air or to some mechanical change in the materials of the system, they clearly indicate that slow chemical changes were taking place. It seemed possible that the oxygen of the air, dissolved in the cadmium sulphate solution, might have oxidized the mercurous sulphate to the more soluble mercuric compound and,

if the rate of this oxidation was more rapid than the subsequent rate of reduction by the mercury, the observed results could be readily explained. This possibility had been considered¹ and reasons given for rejecting it, but in view of the importance of the results obtained by rotating the cathode systems of standard cells, it has seemed advisable to further test the possibility of an effect due to the dissolved air. The test was carried out with apparatus similar to that used in the previous experiment. An adjustable cell (Fig. 1) was constructed from the materials which were to be tested in the rotating tubes. This cell was kept at 25° and, although the anode leg was frequently removed to test other systems, the cell has not varied over .00001 V. from its value of 1.01838 V. The rotating tubes are represented by Fig. 2.

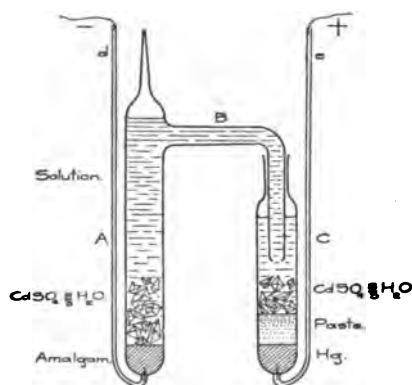


Fig. 1.

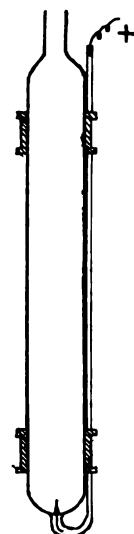


Fig. 2.

the platinum contact wire was sealed through the bottom of the tube, extended 8 mm. up into the tube where it was covered with a thin sheath of glass except for 2 mm. of the end which was exposed and thoroughly amalgamated. A small glass tube was passed over the end of the platinum wire which was outside of the tube, and then sealed to the large glass tube. This little glass tube

¹PHYS. REV., 23, 180.

was bent as indicated in the figure and served to protect and insulate the copper lead wire. Contact between the platinum and copper wires was made with a little mercury and the rest of the little tube was filled with wax. The rotating tubes used were 20 mm. in diameter and 200 mm. long, each contained 7 c.cm. of mercury, 4 c.cm. of mercurous sulphate, 4 c.cm. of powdered cadmium sulphate and about 50 c.cm. of the saturated solution. These two systems were alike in all respects except that the air was rigorously excluded from tube No II. while tube No I. contained air and was frequently opened.

These tubes with their contents were rotated about their longer axis in the 25° bath just as described² for the first experiments. The temperature of 25° was determined by certified $1/50^{\circ}$ thermometers and the large 100 liter thermostat seldom varied $.02^{\circ}$ from this temperature. Care was exercised to keep the bath covered so as to protect the rotating system from the action of light since the black product, formed by the action of light on mercurous sulphate, increases the mercury concentration of the solution.

The materials used were distilled mercury,¹ recrystallized cadmium sulphate (the clear crystals only were used), and a saturated solution of these crystals. The mercurous sulphate was prepared chemically by adding an acid solution of mercurous nitrate to a 1 to 6 sulphuric acid solution. The sulphuric acid contained mercury and was rapidly stirred while the mercurous nitrate solution was added drop by drop. In the first experiments the gray electrolytic mercurous sulphate was used (l. c.) while here the chemically prepared sample was white, distinctly crystalline and coarse-grained. The preparation was brought onto a Gooch crucible, washed with sulphuric acid ($D=1.15$), with absolute alcohol to remove the acid, and finally with the saturated cadmium sulphate solution. Particular attention was given to these washings, because it had been found that sulphuric acid prevented the changes under consideration. The washed mercurous sulphate was mixed with an equal bulk of powdered cadmium sulphate crystals and brought into the rotating tube No. I., which already contained the mercury and

¹ *PHYS. REV.*, 23, 177.

² *PHYS. REV.*, 21, 387.

saturated solution. This tube was closed with a cork and a rubber cap and was rotated in the bath.

Tube No. II. was first charged with the mercury and powdered cadmium sulphate and then evacuated and filled with pure hydrogen gas. The tube was evacuated and refilled with hydrogen several times in order to make sure that all the air had been removed from the tube and its contents. The saturated cadmium sulphate solution was brought into a vacuum and shaken until the dissolved air had been practically removed. Hydrogen gas was then allowed to bubble through the solution for three days. The mercurous sulphate was washed as before except the final washings were made with the hydrogen saturated solution and care was taken to avoid drawing air through the sulphate. This sulphate was washed into tube No. II. with some of the hydrogen saturated cadmium sulphate solution, a current of hydrogen prevented the entrance of air and after the tube had been nearly filled with the solution it was evacuated and sealed off before the blow pipe. The materials of this tube No. II. may have retained some hydrogen but they were free from oxygen and when the tube was opened, after two weeks' rotation, the vacuum was still in evidence so there could have been no leak.

The tubes were rotated together and at the same rate. After 33 hours, the rotation was stopped, tube No. I. was brought to an upright position and measured with the anode leg of the adjustable cell.

3 minutes after stopping the rotation the E.M.F. was	1.01960
6 " " " " " " " "	 51
13 " " " " " " " "	 40
45 " " " " " " " "	 30
60 " " " " " " " "	 29

The rotation was then continued and after 4 days the observations were,

2 minutes after stopping the rotation the E.M.F. was	1.02036
5 " " " " " " " "	 17
10 " " " " " " " "	 08
20 hours " " " " " " " "	1.01986
60 " " " " " " " "	 77
6 days " " " " " " " "	

The rotation was then continued for 6 days making a total of ten days and tube No. I. was again tested.

2 minutes after stopping the rotation the	E.M.F. was	1.02035
8 " " " " " " " "		 18
45 " " " " " " " "		 09
2 hours " " " " " " " "		 05
6 " " " " " " " "		 00
Adjustable cell.....		1.01838

Evidently the system had about reached its maximum value and was nearly .00200 V. higher than the adjustable cell which had been made from the same materials. The increase in E.M.F. was somewhat greater than in the first experiments but the maximum value obtained has no real significance since it is not an equilibrium point; otherwise there would have been no change after the rotation was stopped. The significance of the decreasing E.M.F. will be considered later, here attention may well be called to some features of the experiment. The adjustable cell was compared with the standards before and after each series of measurements on a rotated system and since there was no variation of the adjustable cell greater than .00001 V., it is certain that the anode tester remained constant and that the observed changes were all in the rotated system. Furthermore, after the solids had settled in the rotated tube, some of the clear supernatant solution was removed, and tested on a clean mercury electrode with the adjustable anode and the value 1.02013 V. was observed. We may therefore be quite confident that the large values obtained for the E.M.F. were due solely to an increase in the mercury concentration of the rotated solution.

Tube No. I. had about reached its maximum value but was again rotated and two days later when both tubes had been rotated a total of twelve days, the hermetically sealed tube No. II. was also tested with the anode leg of the adjustable cell.

The agreement between the two tubes is as good as between different measurements on tube No. I., and since the systems were not in equilibrium the agreement in maximum values is better than was to be expected. The decreasing values depend for one thing on diffusion and this rate of decrease varied at different times for the same system as may be seen from the various measurements on tube No. I. The results obtained, therefore, give a decisive answer to the question at issue and we may conclude that the dissolved air plays no rôle in these rotation experiments.

Time from Stopping the Rotation.	Tube No. II. Air Free.	Tube No. I. Air Saturated.	Time from Stopping the Rotation.	Tube No. II. Air Free.	Tube No. I. Air Saturated.
1½ minutes.	1.02040 V.	1.02060	24 hours.	1.01972	1.020000
2 "	23		2 days.	60	1.01988
5 "	11	50	4 "	46	64
10 "	03	42	7 "	34	40
30 "	1.01997	36	14 "	12	16
60 "	91	33	21 "	00	
3 hours.	86	22	30 "	1.01800	
6 "	81	17			

Since the dissolved oxygen did not cause the changes in the cathode system, there must have been some interaction between the materials of the rotated tubes which increased the mercury concentration of the solution. If this action was hydrolysis, as has been suggested, an explanation of the observed changes would be possible. Assuming that hydrolysis did take place it followed that the presence of sulphuric acid, one of the products of hydrolysis, would minimize or prevent the changes. This conclusion was tested by the following experiment :

A saturated solution of cadmium sulphate was made tenth molecular in respect to sulphuric acid and this acid solution was used in constructing an adjustable cell and in filling a rotating tube. Electrolytic mercurous sulphate was washed with alcohol and with the acid cadmium sulphate solution and was then made to a paste in the usual way. The other materials, apparatus and method were the same as for the preceding experiments. The adjustable cell, due to the presence of acid, was lower than the cadmium cell (1.01825 V. at 25°), but quite as constant. The cathode system in the tube was rotated as previously described at 4 r.p.m. and after twelve hours it was measured with the anode leg of the adjustable cell with results as follows :

3 minutes after stopping the rotation the E.M.F. was.....	1.01812 V.
8 " " " " " " " " " "	22
30 " " " " " " " " " "	22
60 " " " " " " " " " "	22
Adjustable cell.....	24

After two days rotation the following results were obtained :

2 minutes after stopping the rotation the E.M.F. was	1.01815
5 " " " " " "	20
20 " " " " " "	24
10 hours " " " " " "	24
Adjustable cell.....	25

The tube was then rotated two weeks :

2 minutes after stopping the rotation the E.M.F. was	1.018200
4 hours " " " " " "	21
12 " " " " " "	22
3 days " " " " " "	25
4 " " " " " "	23
Adjustable cell.....	24

This system — mercurous sulphate, mercury, cadmium sulphate and acid solution of cadmium sulphate — came to equilibrium soon after it was brought together and there was then no further change. The system behaved exactly as did the cathode system of the Clark cell.¹ The effect of the sulphuric acid in eliminating the changes in the rotated system is in agreement with the view that the neutral cadmium sulphate solution hydrolyzed the mercurous sulphate, but this is not by itself a proof of the point.

This experiment, with the previous ones, furnishes more evidence on the question of oxidation by dissolved air. The materials and solution in this last experiment were air saturated and frequently opened to the air but the system came to equilibrium at once with the normal E.M.F. This would hardly have been the case if the dissolved air had been oxidizing the mercurous sulphate. In the rotation experiment with the cathode system of the Clark cell the zinc sulphate solution was air saturated, but did not oxidize the mercurous sulphate because the system showed the normal value and did not change on continued rotation.²

It will be seen that the experiment just described also gives some

¹ *PHYS. REV.*, 23, 181.

² The work of J. W. McBain (*J. Phys. Chem.*, 5, 621, 1901) on the oxidation of ferrous solutions by free oxygen, may be mentioned in this connection. The author found that the rate of oxidation of ferrous sulphate by dissolved air was proportional to the square of the concentration of the ferrous sulphate proportional to the concentration of the oxygen, and that sulphuric acid had only a slightly retarding influence on the rate. The rate was unexpectedly slow, it was shown that precautions prescribed in volumetric analysis for preparing a ferrous sulphate solution from iron wire are quite unnecessary, since with air bubbling through the solution only .05 per cent. of ferric iron was formed

evidence on the question of the size of particles changing the solubility of the mercurous sulphate. A fine powder has an abnormally great solubility but the effect has not been observed until the powder contained a large number of particles with diameters less than one or two microns.¹ Previous experiments have shown that mercurous sulphate which settled rapidly in a 1 to 6 sulphuric acid solution was sufficiently coarse-grained to avoid a measurable effect of the size of the particles on the solubility. But the mercurous sulphate might have been ground to a fine powder in the rotating tubes and this would not only have increased the mercury concentration of the solution, but on standing, the finer more soluble crystals would have disappeared and the mercury concentration would then have decreased. The changes in E.M.F. observed on rotating the cathode system of the cadmium cell corresponded with this explanation, but when a little acid was added the system soon came to equilibrium and the slow changes previously observed were entirely lacking. The same kind of mercurous sulphate and rate of rotation were used in both cases so the observed changes in the first experiment cannot be explained as due to finely divided particles or to grinding of the solids since the presence of the acid in the last experiment could not have effected either of these factors.

The electrolytic mercurous sulphate and the same rate of rotation were used in the experiment with the cathode system of the Clark cell, the system came to equilibrium at once with no changes characteristic of the presence of finely divided particles and the same conclusions may be drawn from that experiment. The method of rotating the tubes² was devised in order to avoid grinding the solid contents of the system but at the same time it was necessary to insure a thorough mixing of the cathode materials and this was satisfactorily accomplished by the method and apparatus employed.

THE AGING OF STANDARD CELLS.

In the method of constructing cells devised by Clark,³ Wright and Thompson⁴ and Rayleigh,⁵ the mercurous sulphate was washed

¹ *Zeit. Phys. Chem.*, 49, 385, 1901.

² *PHYS. REV.*, 23, 177.

³ *Proc. Roy. Soc.*, 20, 444, 1872.

⁴ *Phil. Mag.*, 16, 25, 1833.

⁵ *Phil. Trans.*, 175, 411 and 176, 781, 1886.

with water and thus contained the basic salt even if it had not been previously formed in making the mercurous sulphate. Such cells always had a high value (1 to 2 per cent., Rayleigh, l. c., 446) and required a month or two of "aging" before they reached a constant value. On the other hand when the mercurous sulphate was properly prepared and washed so as to exclude the basic salt from the depolarizer,¹ the cells had their constant value at once. Cells have been made with depolarizers which contained known amounts of the basic mercurous sulphate and these cells had a high preliminary value, and then showed the characteristic decrease. Electrolytic mercurous sulphate was shaken with definite amounts of water and an excess of mercury, thus a definite amount of the basic salt was formed and mixed with the undissolved solid. This mixture was made to a paste in the usual way, cell A44 contained one per cent. of the basic salt in the depolarizer, cell A45, three per cent., and cell A46, 10 per cent. while the completely hydrolyzed salt ($2(\text{HgOH})\cdot\text{Hg}_2\text{SO}_4$) was used for cell A41. These cells have been maintained constantly at 25° and their records for over a year are as follows.

Cell.	Jan. 13.	Jan. 26.	Feb. 7.	March 13.	April 13.	May 12.	June 4.
A44	1.01878	1.01871	1.01868	1.01866	1.01865	1.01862	1.01860
A45	64	60	58	55	53	52	47
A46	98	90	86	80	74	69	62
A41	1.01768	760	767	774	776	772	770
Cell.	July 7.	Aug. 14.	Nov. 15.	Dec. 19.	Jan. 3.	Feb. 26.	
A44	1.01857	1.01855	1.01853	1.01854	1.01850	1.01849	
A45	47	47	45	57	46	46	
A46	57	56	44	40	40	44	
A41	764	756	747	741	736	732	

The cells with one per cent. and three per cent. of basic salt have become fairly constant, while cell A46, with 10 per cent. of basic salt in the depolarizer, had the highest preliminary value and has varied the most while the cell with only the basic salt, A41, shows no sign of becoming constant. The depolarizers of cells A35 to A40² were made basic by mixing known amounts of the completely hydrolyzed salt with the normal salt. The effect was not as great

¹ PHYS. REV., 23, 172.

² PHYS. REV., 22, 328.

as in the experiments just described but of the same general character. The higher values and more rapid rate of decrease were found in the case of the cells with the larger per cent. of basic salt, and these cells were liable to go below the normal value.

On rotating the cathode system of the cadmium cell an increase in the E.M.F. was obtained and when the system was allowed to rest the E.M.F. began to decrease, rapidly at first and then at a decreasing rate. The mercurous sulphate which had been rotated thirty days with the cadmium sulphate solution and mercury was used as the depolarizer of cells A49 and A50 (p. 17), and these cells had a high value and then decreased and are now below normal value and still decreasing. The parallelism between all these facts is evident and indicates that a basic mercurous sulphate was formed in the rotation experiments. The fact that a little sulphuric acid prevented the changes in the cathode system is in agreement with this view and on the whole it seems reasonable to conclude that a neutral cadmium sulphate solution interacts with the depolarizer to form a basic mercurous sulphate. Hydrolysis would account for the facts established by the previous experiments, but the basic salt formed by the action of the cadmium sulphate solution is probably different from the one formed by the action of water, otherwise we would expect the cells with variable amounts of the basic salt (due to water) to show more agreement since it would be a case of two solids saturating a solvent and enough of the basic salt to prevent any action of the cadmium sulphate solution. But whatever the nature of the new phase which formed on rotating the cathode system of the cadmium cell, the subsequent decreasing E.M.F. showed that the system had not attained equilibrium.

There evidently were two oppositely directed changes taking place; the one, assumed to be hydrolysis of the mercurous sulphate, increased the mercury concentration of the solution while the other and much slower change was evidently a secondary action of the mercury on the soluble products of hydrolysis. This secondary action occurred only when the basic salt was or had been present and it caused a decrease of the mercury concentration of the solution. Tube No. I. attained the high value of 1.02060 V. and on standing, decreased to 1.01900 V. in three weeks but on examining the super-

natant solution it was found to have still retained a high value showing 1.02013 V. against a mercury electrode. This test was made by bringing some of the clear liquid onto a mercury electrode in a little tube like the part (C) of Fig. 1 and measuring the E.M.F. with the adjustable anode. When left in contact with the mercury electrode the clear liquid showed a slowly decreasing value and shaking it with the mercury seemed to have very little effect in hastening the action.

First reading	1.02013
6 minutes	00
20 "	1.01998
90 "	89
1 day	68
3 days	51
10 "	49

We may therefore conclude that, both in the cells which contained basic salt and in the rotated systems, there was a slow secondary reaction which took place and that this action *was only at the surface of the mercury*. The rate at which the mercury concentration of the solution above the paste decreased depended on the rate of diffusion of the solution through the paste and thus depended on the mechanical fineness of the solid materials of the cathode system. The hydrolysis, or whatever reaction formed the basic salt, could not have attained equilibrium until the secondary action was completed or had formed a new phase. If this view is correct it is probable that the maximum value was not observed in any of the rotation experiments. In the first experiment with the gray electrolytic mercurous sulphate there was a tendency for the mercury to become divided into fine globules, and thus the mercury surface was much increased and consequently the rate of the secondary reaction. In the experiment with the white chemically prepared mercurous sulphate (p. 19) there was no tendency of the mercury to become finely divided and the maximum value was higher than in the first experiment and attained in less time. Evidently variations in the materials and in the apparatus and method used will give quite different results, but the experiments seem to clearly show that in the cathode leg of the cadmium cell we have a system which is in unstable equilibrium.

The changes that have been observed in the E.M.F. of cadmium cells are of course small compared to those obtained in the rotation experiments. The F series of 10 cells which were made February 15, 1904, showed an agreement among themselves of one part in 100,000 for nearly a year, but now they show variations of 5 parts in 100,000 and are from 10 to 15 parts lower than they were when made. The A series of October 21, 1905, showed the same excellent agreement for nearly a year.

Cell.	Oct. 26.	Dec. 14.	March 4.	June 4.	Oct. 2.	Dec. 19.	March 18.
A1	1.01843	1.01843	1.01843	1.01842	1.01842	1.01841	1.01841
A2	42	43	43	42	46	44	43
A3	42	42	43	42			
A4	43	43	43	42	42	42	42
A5	43	43	43	42	41	40	40½
A6	43	43	43	43	42	42	42

The paste in these (A) cells was about 2 cm. deep and the cells have remained undisturbed in the 25° bath, but are not now in as good agreement as formerly, although they have not shown as great a decrease as was exhibited by the F series.

It is probable that cadmium cells, made with a fine-grained depolarizer of good depth, would show less variations than have been shown by the F and A series, since there would be less chance for diffusion and consequently for the changes indicated in this article. A very fine-grained mercurous sulphate retains the sulphuric acid very tenaciously, and the presence of this acid in the cell also tends to retard the changes. But a standard cell which depends on the mechanical conditions of the solid materials and is in unstable equilibrium must be less reproducible and less constant than cells which are free from these defects. In the experiment in which acid was added to the cathode materials of the cadmium cell it was found that the system soon came to equilibrium, and this has suggested that the cadmium cell should have a definite amount of sulphuric acid. A number of these acid cadmium cells have been constructed and are very constant, but as yet insufficient observations have been made on them to judge of their worth.

At the same time the F and A cells were made, Clark cells were also made and with depolarizers made from the same samples of

mercurous sulphate as served for the cadmium cells. These Clark cells are now in good agreement and have the same value as cells made in the last few months from fresh materials. This is in agreement with the results of the rotation experiments on the cathode systems of the Clark and cadmium cells.

The fact that these Clark cells which were made at various times with fresh materials are now in good agreement ($\pm .00002$ V.) is proof that they have not changed and that they form a reliable basis of electromotive force. The absolute value of these cells is 1.4204 volts at 25° , as determined by Dr. K. E. Guthe.¹

The essential points to be observed in constructing these cells have been given.² The high temperature coefficient of the Clark cells have made it necessary to have very constant temperature baths. A large copper tank contained 100 liters of kerosene oil and was electrically heated and controlled. A mercury-toluene regulator operated the relay, which in turn controlled the heating current. This regulator consisted of glass tubes joined together in the form of a gridiron so as to be well distributed in the bath. The tubes were filled with toluene, except the outlet, which was filled with mercury. Contact with the relay circuit was made with a very fine platinum wire (.05 mm.), and a condenser was used to prevent sparking. It was found that with the very fine contact wire there was no "fouling" of the mercury and no "drift" of the bath temperature. The heating coils were also in the form of a gridiron, made of glass rods and pianoforte wire, which was wound on the glass rods and then thoroughly shellacked. The resistance was 120 ohms and the heating current was only one half ampere (an alternating current was used). The heating surface was large and well distributed in the bath, and only a very small amount of heat was needed, because the bath was well protected with non-conducting materials. The oil was stirred with a motor-driven paddle and there were no differences of temperature in the various parts of the bath that could be detected with a Beckmann thermometer. The temperature was determined by certified $1/50^{\circ}$ thermometers, and these thermometers were checked at the transition point of sodium

¹ Bull. Bur. Standards, 2, 33, 1906.

² Phys. Rev., 22, 334-338.

sulphate, 32.383° .¹ An Otto Wolff potentiometer was used in the measurements, and its corrections were known and applied when necessary. The galvanometer gave 2 mm. deflection for .00001 V. In making measurements it was found best to join all the anodes of all the cells together, and particular attention was given to the question of insulation. The measurements given are regarded as correct to the .000005 V.

PRINCETON UNIVERSITY,

March 15, 1907.

¹ Richards & Wells, *Zeit. Phys. Chem.*, 43, 471, 1903.

CRYSTAL RECTIFIERS FOR ELECTRIC CURRENTS AND ELECTRIC OSCILLATIONS.

PART I. CARBORUNDUM.

BY GEORGE W. PIERCE.

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Introduction. — General H. H. C. Dunwoody of the United States Army has discovered¹ that a crystalline mass of carborundum when supplied with electrodes acts as a receiver for electric waves. In his patents specification General Dunwoody shows several ways of attaching the electrodes to the crystal. One method is to wind the wires around the two ends of the specimen. Another method is to hold the crystal in a clamp of which the two jaws, insulated from each other, serve as electrodes. The crystal with its electrodes is put into a receiving circuit of a wireless telegraph system with a telephone and battery about the carborundum. The sounds heard in the telephone when a message is being re-

¹ U. S. Patent, No. 837,616, issued December 4, 1906; application filed March 23, 1906.

ceived are like those heard with the electrolytic detector. General Dunwoody also found that the battery could be omitted and the leads of the telephone connected directly about the terminals of the carborundum, and with this arrangement, without the battery, he says that he has read messages from a sending station several hundred miles away.

The present investigation was undertaken in the effort to obtain further knowledge of this interesting property of carborundum. The experiments were extended to include many other crystalline substances, but the present discussion is chiefly confined to carborundum.

Apparatus for Current-voltage Measurements.—Fig. 1 shows a sketch of a form of circuit employed in studying the conductivity of carborundum under various conditions. The crystal of carbo-

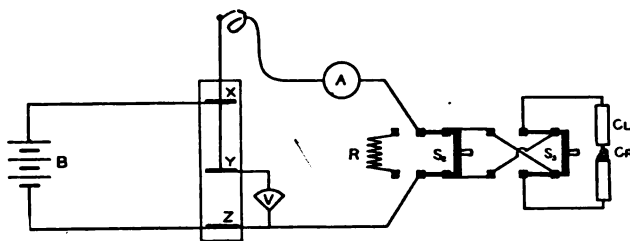


Fig. 1.

rum, held in a clamp, is shown at *Cr*; *B* is a storage battery; *XYZ* is a potentiometer consisting of two fixed plates of zinc *X* and *Z*, and one movable plate *Y*, immersed in a zinc sulphate solution. By means of the voltmeter *V* the difference of potential between the plates *Y* and *Z* could be read, and the resulting current through the carborundum was given by a galvanometer or milliammeter at *A*. The resistance of the galvanometer was so small in comparison with the resistance of the carborundum that the reading of the voltmeter was practically the drop of voltage in the carborundum.

The switch *S*₂ enables the observer to reverse the current in the crystal under examination without reversing the galvanometer. A known resistance at *R*, could be thrown into circuit with the galvanometer for the purpose of calibrating it.

This method of experimenting has previously been employed by Eccles,¹ Guthe and Trowbridge² and others in the study of the coherer; by Rothmund and Lessing³ and by Austin⁴ and Armagnat⁵ in the study of the electrolytic detector.

Current-voltage Curve for Carborundum.—A curve obtained by plotting the current against voltage in an experiment with carborundum is shown in Fig. 2. It is seen that the current through the carborundum is not a linear function of the voltage about it; the apparent resistance of the substance diminishes with increasing current. Curves of approximately this form were obtained by Greenleaf W. Picard⁶ in a study of carborundum. This curve also resembles closely the curves obtained by Rothmund and Lessing, by Austin and by Armagnat for the relation of current to voltage in the electrolytic receiver. It resembles also the building up portion of the current-voltage curve in the coherer as obtained by Eccles.

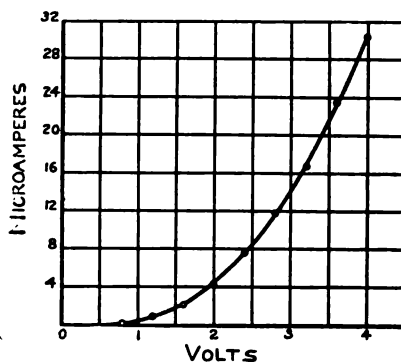


Fig. 2.

Experiments were made by the writer on a great many specimens of carborundum, and curves of approximately the shape shown in Fig. 2 were obtained in all the cases. The value of the current for a given voltage was found to depend on the temperature, and pressure, and on the method of leading the current to the crystal, and was different for different specimens. Before discussing these effects of temperature, pressure, etc., attention is called to a more interesting property of carborundum, the property of unilateral conductivity.

Unilateral Conductivity of Carborundum.—The current through the crystal in one direction under a given electromotive force was

¹ Electrician, 47, pp. 682 and 715, 1901.

² Phys. Rev., 11, p. 22, 1900.

³ Ann. d. Phys., 15, p. 193, 1904.

⁴ Bureau of Standards, 2, p. 261, 1906.

⁵ Bull. soc. française, Session of Apl., 1906, p. 205.

⁶ El. World, 48, p. 994, 1906.

found to be different from the current in the opposite direction under the same electromotive force; that is to say, carborundum is unilaterally conductive. This effect may be seen by a reference to

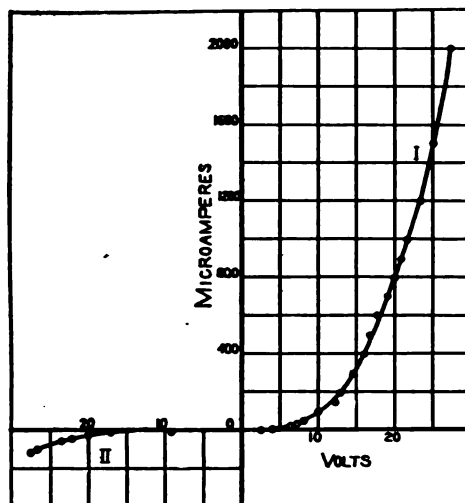


Fig. 3.

Fig. 3. The branch *I* of the curve shows the current, plotted against voltage, when the current is in one direction; branch *II* the corresponding values of the current obtained when the voltage is reversed. The accompanying table, Table I., contains the numerical values from which these curves were plotted. This property of unilateral conductivity of carborundum has been overlooked by previous experimenters on this substance. The property of unilateral conductivity has, however, been previously found in some of the crystalline metallic oxides and sulphides, by Ferdinand Braun. Reference to Braun's work is given in the historical note on page 58. None of the substances investigated by Braun showed such striking asymmetry as that obtained in the present experiments with carborundum.

In the experiment whose result is shown in Fig. 3 and Table I., the specimen of carborundum was held in a clamp under a pressure of about 500 grams, and it is seen that the current in one direction is 100 times as great as the current in the opposite direction when

an electromotive force of 10 volts is applied in the two cases. With increase of current through the specimen, the ratio of the current in the two opposite directions diminishes. At 27.5 volts C_1 is only 17 times C_2 .

TABLE I.

Relation of Current to Voltage, Showing unilateral Conductivity of Carborundum.

Volts.	Current in Microamperes.		C_1/C_2 .
	C_1 , Commutator Left.	C_2 , Commutator Right.	
2.2	1		
2.8	2		
4.0	5		
4.7	10		
5.9	20		
6.5	30		
7.3	40		
8.0	50		
10.0	100	1	100
12.1	150		
12.8	200		
14.5	300	5	60
16.0	400		
16.8	500	10	50
17.7	600		
19.4	700		
20.0	800	20	40
21.0	900		
21.9	1,000	30	33
23.2	1,200	50	24
25.0	1,500		
27.5	2,000	120	17

In this particular experiment the piece of carborundum was submerged in an oil bath designed to keep the temperature of the specimen constant. The piece of carborundum was held in a clamp, the jaws of which served to lead the current to the specimen. The oil of which the temperature was 64°C., came freely into contact with the crystal.

Similar effects were obtained at various temperatures between -10°C. and 100°C., both with and without the use of oil as a bath. A like result was had with different specimens and under different pressures. The relative values of the positive and nega-

tive currents, however, varied from piece to piece, and also was different under different conditions of temperature and pressure. The effects of temperature and pressure are investigated below.

An interesting property of some of the specimens is presented in Fig. 4. The curve of current against voltage obtained when the

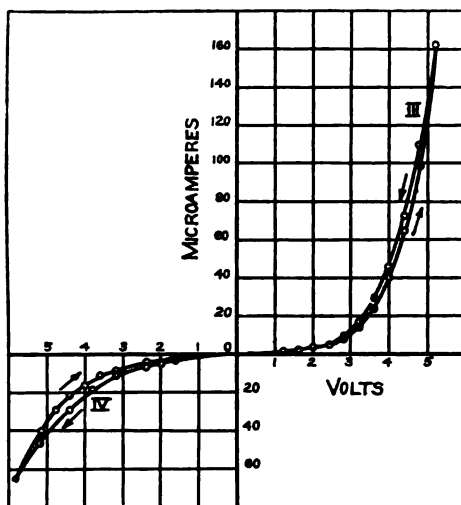


Fig. 4.

voltage was *increased* step by step did not exactly agree with the values of the current obtained with the same voltage when the voltage was *decreasing* step by step. The difference is indicated by the non-coincidence of the two curves marked *III* in Fig. 4. The arrows indicate the order of succession of the observations. Curve *IV* shows the corresponding effects when the current is in the opposite direction. This effect was apparently due to a slow building up of the current, and after several reversals of the current usually disappeared. The specimen that gave the curves of Fig. 4 was under a pressure of 2 kilograms.

Effects of Pressure.—Current-voltage curves were taken with the same specimen under various pressures. A series of results are shown in the curves of Fig. 5. In taking these observations the specimen was held in a clamp with jaws insulated from one another. One of the jaws was capable of being moved forward without rotation under the action of a screw and spring. The spring was cali-

brated, so that the pressure on the carborundum could be read off on a scale. Care was taken that the specimen was subjected to a steady compression without twisting. The pressure was in the direction of the current.

In taking the set of observations shown in Fig. 5 the pressure was first made three kilograms, giving the top curve of the series. The pressure was then reduced successively to two kilograms and one kilogram. From the first quadrant of the figure it is seen that

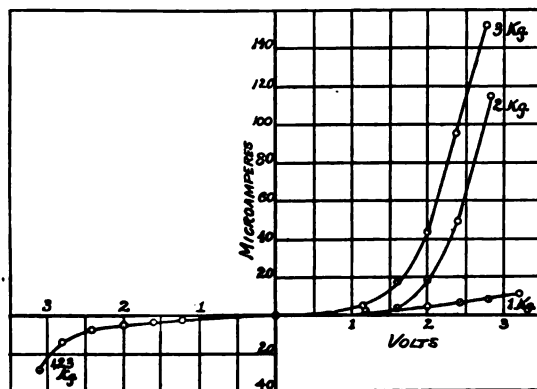


Fig. 5.

the conductivity of the specimen diminishes with diminishing pressure. This is the case when the current is in one direction. With the current in the opposite direction the current-voltage curves for the three different pressures coincide, and for the case of the pressure equal to one kilogram the prevailing conductivity is actually reversed with respect to its direction in the case of the higher pressure.

Several experiments were made with other specimens of carborundum with considerable disparity in the results, and the curves of Fig. 5 cannot be taken to represent a general occurrence.

Many of the results of the experiments here described are apparently confused by difficulties arising at the contact of the metallic electrodes with the crystal. On account of the irregularities of the surfaces of the specimens actual contact with the electrodes in general occurs at small areas. Although this contact is apparently not loose when the pressure on the clamp is several kilograms, it is

evident that the carborundum, which is an exceedingly hard substance, will imbed itself in the electrodes to a depth depending on the pressure, and one cannot be certain that a specimen will return to its original condition when the pressure is put on and taken off or when the specimen is removed from the clamp and again replaced in it. On this account the experiments are sometimes incapable of repetition unless the clamp is left undisturbed.

Experiments with Platinized Specimens of Carborundum.—In the effort to avoid these difficulties and in the effort to ascertain what part the form of contact plays in the phenomenon of unilateral conductivity in crystals, a number of specimens of carborundum were selected with opposite faces plane and very approximately parallel. The faces thus found were parallel to the natural hexagonal base of the crystal, and were in several cases apparently the natural crystal faces.

Some of the parallel-faced crystals were platinized on one or both of their smooth surfaces by the cathode discharge so as to make firm contact with the electrodes. The metallic surfaces thus obtained were in many cases optically plane, as evidenced by the fact that when used as mirrors they did not appreciably distort the image. The platinized faces were put in contact with the electrodes. The current in these cases was perpendicular to the crystal base.

Platinized on One Face Only.—Some of the specimens, platinized on one face only, gave very remarkable unilateral conductivity. A specimen, called Carborundum 11, was platinized and broken into two parts. Table II. and Table III. show results obtained with one of these parts designated 11_b. This specimen was .6 mm. thick, with area of about 1 sq. mm. One of the faces, which was optically true, was heavily platinized. The other face was somewhat rough and was without platinum. The specimen was held in a clamp with silver jaws. Careful examination showed that the rough, unplatinized face of the crystal made contact at only a few points with the electrode on that side. Four different pressures were used, 350 grams, 1 kg., 2 kg., and 3 kg. With a given voltage the current toward the platinized face was in each case *greater* than the current in the opposite direction.

For a pressure 350 grams, recorded in Table II., and for voltages

below 20 volts, the current from the platinized face gave no appreciable deflection of the milliammeter, of which one division was 3.92 microamperes, while the current toward the platinum was 172 microamperes at 20 volts. At 22 volts the current from the platinum was .39 microamperes, while the current in the opposite direction was 910 times as great. At 34.5 volts the current toward the platinum was 527 times the current from the platinum.

TABLE II.

*Crystal 11. Thickness .6 mm.; Area 1 sq. mm. Platinized on one side.
Pressure 350 Grams.*

Volts.	C_1 , Current toward Platinum in Microamperes.	C_2 , Current from Platinum in Microamperes.	C_1/C_2 .
10.5	3.92		
14	11.8		
15	25.5		
17	55		
20	172		
22	355	.39	910
23	520	.60	850
25	850	1.06	800
30	1,920	3.05	630
34.5	3,100	5.90	527

Pressure 1 Kg.

Volts.	C_1 .	C_2 .	C_1/C_2 .
4.5	3.92		
6	7.84		
7	19.6		
9	39.2		
10	64.0		
11	98.0		
13	168		
15	282		
16	350		
18	600		
21	1,000		
26	2,000		
30	3,000	.75	4,000
34.5	4,200	3.92	1,070

TABLE III.

Same Specimen as Table II. Pressure 2 Kg.

Volts.	C_1 , Current toward Platinum in Microamperes.	C_2 , Current from Platinum in Microamperes.	C_1/C_2 .
4.2	3.92	.00	
5.8	7.84	3.92	2.0
7.0	19.6	4.70	4.2
8.1	39.2	9.4	4.2
9.2	78.4	19.6	4.0
10	118	39.2	3.0
11	210	71.0	2.96
12	255	121	2.10
13	380	175	2.18
14	440	260	1.72
15.8	700	350	2.0
17	1,000	420	2.38
21.2	2,000	770	2.6
23	2,500	1,000	2.5
24.5	3,000	1,500	2.65
26.2	3,500	1,360	2.58
28	4,000	1,500	2.66
31.5	5,500	1,900	2.90
34.5	6,700	2,600	2.68

Pressure 3 Kg.

Volts.	C_1 .	C_2 .	C_1/C_2 .
3.5	3.92	.39	10
5	12.6	2.62	4.8
6	23.5	7	3.36
6.8	39.2		
8	78.5	21.5	3.55
9	118	33.2	3.55
10.2	196	78.4	3.52
12.0	314	158	2.00
13	392	240	1.60
14.2	500	392	1.30
15	600	420	1.43
17.5	1,000	700	1.43
20	1,500	1,100	1.36
21.7	2,000	1,400	1.43
24.5	3,000	1,950	1.54
30	4,500	3,300	1.37
34.5	6,700	4,400	1.56

With the pressure 1 kg., also recorded in Table II., the conductive asymmetry of the crystal was still greater, and at 30 volts the current toward the platinized face was 4,000 times the current in the opposite direction. These results for 350 grams and 1 kg. pressure are plotted in the curves of Fig. 6. The current toward

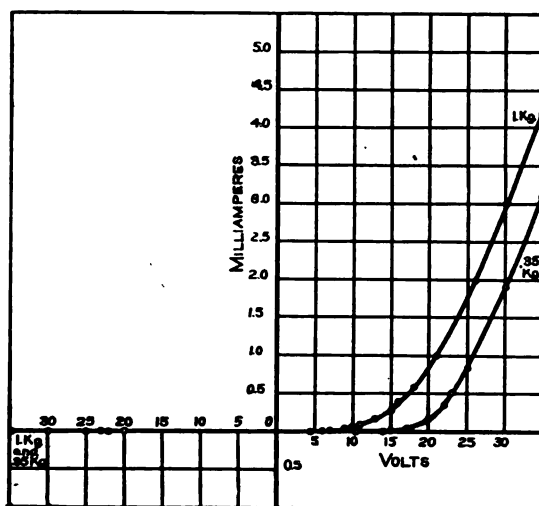


Fig. 6.

the platinized face is given in the right hand quadrant. The current in the opposite direction does not appreciably depart from the axis.

When the pressure was increased to 2 kg., and then to 3 kg. (Table III., Fig. 7) the currents in both directions were increased and the ratio of C_1/C_2 was reduced, so that the current toward the platinum was only two or three times as great as the current in the opposite direction for a given voltage.

The ratio of the current in one direction to the current in the opposite direction is reduced by increasing the pressure on the specimen from 1 kg. to 2 kg. On the other hand, if we examine these two currents with respect to their difference for a given electromotive force, it is seen that the *excess* of one of the currents over the opposite current is increased with increase of pressure.

Another small specimen also broken from crystal 11 platinized on one side gave analogous results. This small piece called 11_a had

a very sharp point at one end and a wider base at the other end. This specimen was only a fine sliver in the form of a pyramid perhaps .5 mm. long, and .2 mm. wide at the base. The platinized side constituted the base. The pressure on it was very great for so slender a specimen, perhaps 3 kilograms, so that the sharp end was

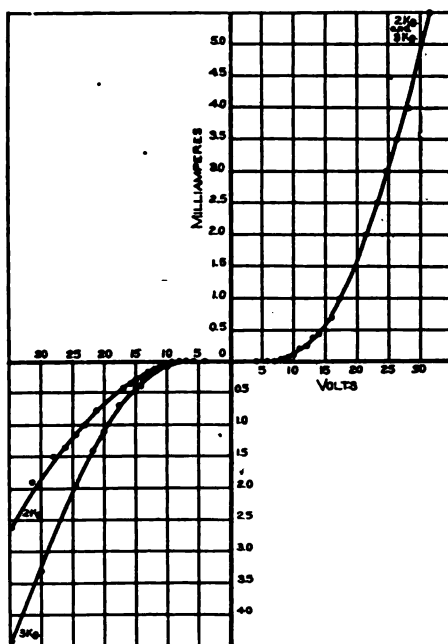


Fig. 7.

driven well into the electrode. The current toward the platinum (base) was again greater than the current in the opposite direction. The ratio of the current C_1 to C_2 in this case was 524 at 18 volts, and 271 and 32 volts.

Carborundum Platinized on Both Sides. — Specimen No. 19 gave the current-voltage values recorded in Table IV. This specimen was .82 mm. thick, had practically parallel plane faces, which were both heavily platinized by the cathode discharge. These flat faces were put into contact with the silver electrodes. The platinum of the edges, which would otherwise short-circuit the crystal, was removed by breaking away the edge of the crystal all around. This left an electrode area to the crystal of about 5 sq. mm. A

pressure of 2.5 kg. was applied to the electrodes, but the amount of this pressure so long as the contact was not evidently loose or so large as to crush the carborundum seemed to have very little effect on the resistance of the specimen.

TABLE IV.

Specimen No. 19, platinised on both sides.

Volts.	Current in 10^{-4} Amperes.		C_1/C_2	Resistance in Ohms.	
	C_2	C_1		R_1	R_2
1	1.5	2.0	1.36	6,660	5,000
1.5	6.0	10.0	1.66	2,500	1,500
2	9.5	15	1.59	2,100	1,330
3	20	30	1.50	1,500	1,000
4	37.9	54.2	1.42	1,060	740
5	68	95	1.40	735	530
6	109	150	1.37	550	400
7	152	210	1.38	455	332
8	217	288	1.33	370	280
9	278	370	1.33	323	243
10	380	485	1.28	263	207
11	460	620	1.35	240	178
12	580	780	1.35	207	154
13	760	970	1.28	171	134
14	920	1,110	1.22	152	125
15	1,100	1,450	1.32	136	103
16	1,350	1,700	1.26	119	94
17	1,650	2,000	1.21	102	85
18	2,000	2,450	1.23	90	73
19	2,500	2,830	1.13	76	67
20	2,940	3,600	1.23	68	55
21	4,200	4,820	1.13	50	43

The ratio of C_1 to C_2 in this table is only about 1.1–1.6, but on account of the low resistance of the specimen, the *difference* between the two currents for a given voltage is large. It should be noted that the current values in Table IV. are given in 10^{-4} amperes, while in the previous Tables the microampere (10^{-6} amperes) was the unit employed. This specimen shows unilateral conductivity with currents up to one half ampere. Up to this value the current through the specimen was also remarkably steady in comparison with the unplatinized specimens. At one half ampere the crystal was considerably heated, so that the massive electrodes in contact

with the specimen became uncomfortably warm to the touch. Under this current the crystal glowed over a small area on both surfaces. Whether this glow was incandescence or a luminescence I am not able to say at present. The glow was examined with a spectroscope, but was so faint that the spectrum has not as yet been clearly made out. All of the specimens of carborundum thus far studied showed this glow at the electrodes when the current was pushed to a high value. Some specimens, apparently inhomogeneous, showed a glow also at a small region in the interior of the crystal. When the glow appeared the measurements were usually discontinued on account of the irregularity of the current readings.

Rectification of Alternating Currents by Carborundum.—In the previous experiments it has been shown that carborundum is unilaterally conductive, giving a greater current in one direction than in the opposite direction when the same electromotive force is applied in the two cases. If this property is manifested for rapid reversals of voltage, an alternating voltage ought to give more current in one direction than in the other. Experiments show this to be the case.

The form of circuit shown in Fig. 8 was designed to permit the employment of either direct or alternating voltage of the same

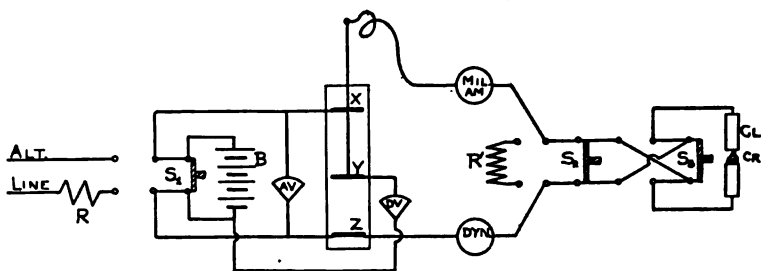


Fig. 8.

value, and to permit the ready measurement of the direct, alternating, and rectified current through the specimen.

The resistance R in the alternating line was adjusted so that the alternating current voltage between X and Z read on the Thomson alternating voltmeter AV with switch S_1 to the left was the same as the direct voltage between these plates when the switch S_1 was thrown to the right so as to put in the battery B instead of the alternating line.

Since the resistance XYZ was non-inductive it was assumed that the drop in potential between Y and Z was the same for either direct or alternating voltage. This drop between Y and Z was read, with the direct current source, on the Weston direct current voltmeter DV .

The resulting current through the crystal Cr was read on both the milliammeter and electro-dynamometer in series with the crystal. With the alternating current source the former gave the rectified current and the latter gave a reading depending on the total alternating current through the specimen.

The specimen used in the experiment was taken almost at random from a beaker full of crystals of carborundum, and though this

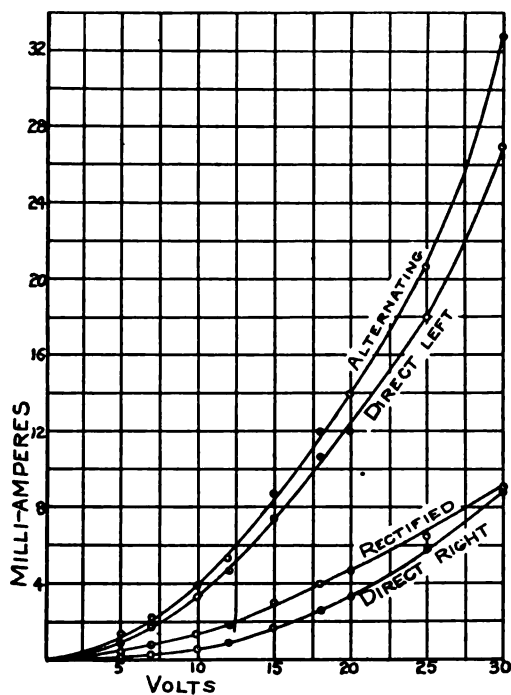


Fig. 9.

specimen does not possess polarity to the remarkable degree exhibited by specimens 11_a and 11_b , it yet shows the possibility of rectifying alternating currents by the use of carborundum. Table V. shows a series of observations which are plotted in Fig. 9. The

table contains the voltage, the direct current in the two opposite directions obtained with the battery as source, the total alternating current as read on the dynamometer, and the rectified current with the alternating source. The alternating current made 60 cycles per second.

In Table VI. one half the difference between the two opposite values of the direct current is put in for comparison with the rectified current. This quantity $\frac{1}{2}(c_1 - c_2)$ is the reading we should have for the rectified current if a steady voltage of which the direction was reversed at a uniform rate were applied to the circuit. We should not expect agreement of the current obtained in this way with the rectified current under alternating voltage, but the fact that the two

TABLE V.

Direct, Reversed, Alternating and Rectified Current for Different Voltages.

Volts.	Current in Milliamperes.			
	Direct Left, C_1 .	Direct Right, C_2 .	A, Alternating.	R, Rectified.
5	.9	.07	1.3	.57
7	1.7	.2	2.21	.98
10	3.22	.52	3.9	1.61
12	4.53	.89	5.22	2.08
15	7.5	1.16	8.8	3.35
18	10.7	2.53	11.7	4.13
20	12.0	3.25	14.0	4.7
25	18.0	5.6	20.7	6.25
30	26.8	8.9	32.7	9.0

TABLE VI.

Efficiency.

Volts.	Rectified.	$(C_1 - C_2)/2$.	R/A .	$\pi R/2A$.
5	.57	.41	.44	.69
7	.98	.75	.44	.69
10	1.61	1.35	.42	.65
12	2.08	1.82	.40	.63
15	3.35	3.17	.38	.60
18	4.13	4.09	.36	.56
20	4.7	4.37	.34	.52
25	6.25	6.2	.30	.47
30	9.0	8.9	.28	.44

sets of values are of the same order of magnitude gives a rough method of predicting the rectified current from the reversed direct currents.

Efficiency of Rectification.—Table VI. contains also data in regard to the efficiency of rectification by carborundum. In the fourth column is the ratio of the rectified current, read on the Weston ammeter, to the total current read on the electro-dynamometer. This, however, does not give the true efficiency because the current is no longer sinusoidal, and therefore the reading of the dynamometer, which is a deflection instrument calibrated with a direct current, does not give, even approximately, the proper value of the alternating current for the comparison. If the rectification were perfect the reading of the dynamometer would have to be multiplied by $2/\pi$ to give the same reading as the direct current ammeter. The fifth column of the table contains the ratio of the rectified current to $2/\pi$ times the dynamometer reading. This also is not the true efficiency, which is, however, perhaps somewhere between the ratios of column four and those of column five.

Since the efficiency is different for different specimens it is perhaps not important to enter into a more accurate discussion in this place.

The results of Tables V. and VI. show that direct reading instruments in series with a rectifying crystal are capable when properly



Fig. 10.

calibrated of reading on alternating current voltage, and are, therefore, capable of being used in the measurement of alternating currents. There is given below a description of an alternating current voltmeter constructed in this way.

The Modification of Wave Form by a Crystal of Carborundum.—In order to find out by a direct method the effect of a unilaterally

conductive crystal on the wave form, when the crystal was used in a circuit with approximately a sinusoidal impressed voltage, photographs were taken with a Braun's cathode tube. The resulting cycle is shown in Fig. 10. For the experiment Professor Trowbridge kindly placed at my disposal his high-voltage storage battery, for use in producing the cathode beam in the tube. It was found that 20,000 volts in series with a water resistance with running water gave a brilliant and steady spot on the fluorescent screen.

Details of the apparatus are shown in Fig. 11. The coils *cc*

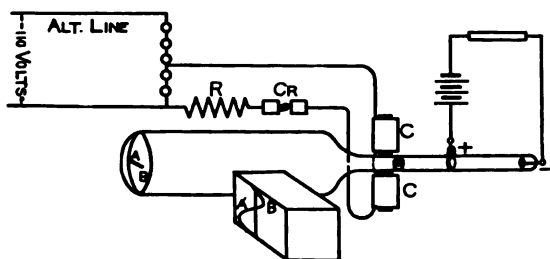


Fig. 11.

for deflecting the beam had together a resistance of about 500 ohms. These coils were provided with cores of soft iron, since it was found impossible to dispense with the iron and have sufficient deflection to show the wave form. The deflecting coils and an additional resistance of 3,720 ohms were in series with the crystal *Cr*. The alternating voltage applied to the circuit containing the crystal was 44 volts, obtained as the drop around two lamps of a lamp-resistance in circuit with the 110-volt line. The crystal was submerged in oil.

The current through the crystal *Cr* and the coils *cc* deflected the cathode beam so that the luminescent spot was spread out in a horizontal line *AB* on the fluorescent screen of the Braun tube. The deflection in one direction was greater than in the opposite direction. Viewed in a mirror revolving with axis horizontal, the fluorescent line was spread out vertically into the wavy line *A'B'*. This curve moved stroboscopically with the mirror. In order to take a photograph the speed of revolution was adjusted to synchronism with the cycle to be photographed. This was done by the adjustment of a conical bearing connecting the motor with the

mirror. The motor was run at approximately constant speed, so that when the coupling was properly adjusted, the image in the mirror could be held stationary for sufficient time to make the exposure (15 seconds.)

The cycle shown in the photograph of Fig. 10 is in form what one might expect from the current-voltage curve previously given. The horizontal line was traced by the spot when the current was shut off, and is therefore the line of zero current. This is the proper axis of the cycle. The mirror was moving at uniform speed so that distances along the axis of the cycle are proportional to the time. The approach of the curve to a horizontal where it crosses the axis is due to the fact that the apparent resistance of the crystal for low voltages is more than the resistance for high voltages. The fact that this effect is shown with the alternating voltage reversing 120 times per second indicates that the change of apparent resistance with the change of current is extremely rapid. If the effect is due to heat, the photograph shows that a marked minimum of temperature coincides in time very closely with the minimum of current. We should perhaps hardly expect the crystal in contact with massive electrodes and submerged in oil to show decided fluctuations of temperature with each fluctuation of the rapidly reversing current.

Another matter for examination in the photograph is the comparative time interval between successive minima of current; that is the comparative time intervals between the zero values of the current on the oscillogram. These intervals are apparently unequal. We cannot, however, be quite sure of this inequality, because on account of the breadth of the band, the positions of these points are somewhat uncertain in the photograph, and if we place the first and second as near together as possible and the second and third as far apart as possible consistent with the picture, the two distances become about equal. If these distances on further experiment should prove to be unequal, we should have evidence of a *persistent* electromotive force in one direction acting to displace the cycle with respect to the axis. This would mean that the rectifying effect was in part an integral effect.

Such an integral effect exists, for example, in the case of a thermo-

electromotive force produced by an electric current, which does not disappear as soon as the current is removed. Also an integral effect arises in galvanic polarization, which does not disappear as soon as the current producing it is removed. So we might expect in the case of the crystal an integral electromotive force persisting in one direction from cycle to cycle. From the picture we cannot say for certain that such a persistent electromotive force exists. If such a persistent electromotive force does exist, it does not necessarily follow that the cause is thermoelectric or galvanic in character.

Experiments on Question of Thermoelectric Origin of Electric Polarity in Carborundum.—Evidence that the action is not thermoelectric is given by the fact that submerging the crystal in oil does not appreciably change its behavior. Also, blowing air over the crystal when it is rectifying an alternating current does not change the current. When used on an alternating voltage, a lighted match held under the piece so as to heat it chiefly at one electrode does not much change the rectified current. These facts seem to be inconsistent with the assumption that the direct electromotive force obtained with an alternating voltage is thermoelectric in origin.

A direct experiment in search of an electromotive force persisting after current was removed was performed as follows. By means of a relay making 60 complete vibrations per second, a direct current from a battery of 35 volts was sent through the crystal of carborundum for intervals of about $1/120$ second, disconnected and a capillary electrometer put about the crystal for alternate intervals of about $1/120$ second. The capillary electrometer gave indications of a persistent electromotive force of less than .002 volt. This is entirely inadequate to account for the unilateral conductivity of the substance, which would require in some cases a back voltage as high as 10 or 15 volts to explain the phenomenon.

After a presentation of the data for other crystals now under investigation, it is proposed to return to a discussion of possible explanations of the phenomenon.

Crystal Rectifiers Employed in the Construction of Alternating Current Measuring Instruments.—On account of the unilateral conductivity of carborundum and certain other crystals to be later

referred to, it is possible by the use of such crystals to adapt an ordinary direct current measuring instrument to the measurement of alternating currents. The utility of these crystals for this purpose will depend upon their permanence and constancy when submitted to long continued use. For this purpose long runs are at present being made.

An alternating current voltmeter making use of carborundum as the rectifying substance has stood satisfactory tests for several weeks. The crystal is put in a metallic clamp enclosed in a tube containing oil, and is used with a delicate Weston milliammeter, with a scale of 100 divisions, each division being 3.92×10^{-6} amperes. Shunt and series resistances as shown in Fig. 12 are used. When these resistances are properly chosen, the scale of the instrument used as an alternating current voltmeter will be nearly uniform over a wide range, or if desired the readings for the small voltages may be spread out instead of being

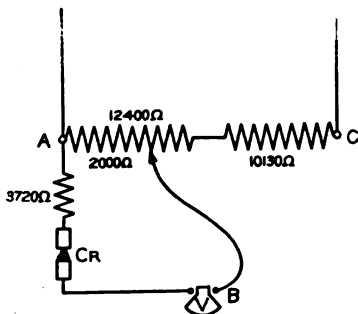


Fig. 12.

compressed as in the ordinary alternating voltmeters. By dispensing with some of the series resistance, or by changing the shunts it is possible to give the instrument a multiple scale.

Calibration curves for the instrument are shown in Fig. 13 and Fig. 14. Curve *I*, Fig. 13, shows the reading of the direct current Weston instrument for different alternating voltages, the instruments being provided with the shunt and series resistances shown in Fig. 12. Curve *II*, Fig. 13, is the corresponding calibration curve without the 10,130 ohms series resistance. The curves are both nearly straight above 20 volts.

When the large series resistances and shunt resistances are omitted and the current sent directly through the 3,720-ohm resistance, the crystal, and the direct current millivoltmeter (resistance 638 ohms), curve *III*, Fig. 14, is obtained. The corresponding direct current curves *IV* and *V* are given in the same figure. With this arrangement the instrument may be read with accuracy from 2

to 10 volts. The deflection at 5 volts alternating is 36 one-hundredths as great as the larger *direct current* with the same voltage, and 7 times as large as the corresponding direct current in the opposite direction. That is to say the loss in sensitiveness of the

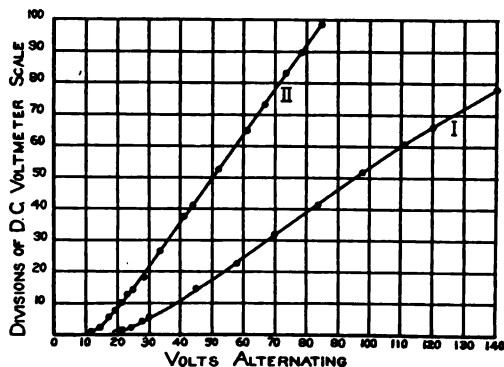


Fig. 13.

direct instrument used on the alternating voltage is not large. Of course, difficulty may in some cases arise in the use of these crystals on account of their high resistance. However, by the use of

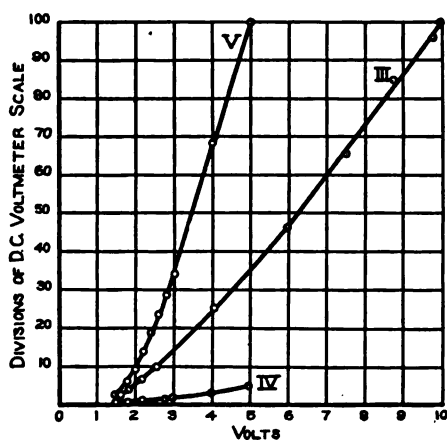


Fig. 14.

a transformer the voltage of an alternating current may be stepped up, and this difficulty avoided. Also by platinizing the specimens, the resistance of the crystal may be greatly reduced.

The alternating voltage used in this experiment made 60 complete cycles per second. Similar measurements with 175 cycles gave substantially the same curves. When used as an alternating current voltmeter, the instrument may be left permanently in circuit without heating or deterioration. The temperature coefficient of conductivity is considered on page 54 below.

The Unilateral Conductivity of Carborundum Used in the Measurement of Telephone Currents.—When it is desired to measure smaller voltages than those given above, a step-up transformer may be used to raise the voltage of the alternating circuit. On account of the high resistance of the carborundum the factor of transformation may be very great, so that the primary of the transformer may be of such small resistance that its introduction into a circuit will not materially modify the conditions of the circuit. In a telephone line a transformer of this kind might quite accurately replace one of the transformers between the talking and listening circuits of the line.

Very feeble currents may be measured in this way, and many experiments on resonance in telephone circuits may be performed. The following experiment serves as an example.

An apparatus similar to that devised by M. Wien, consisting of a rotating wheel carrying iron plugs between the poles of a small permanent magnet, was used to produce a feeble alternating current of 1,440 cycles per second. This alternating current was sent through the primary coil of a telephone transformer. The secondary of this transformer was connected with a delicate ammeter through the crystal of carborundum No. 19, platinized on both sides. A deflection of 16 divisions was shown by the milliammeter. Now the primary circuit was broken and a condenser of variable capacity was inserted in series in the primary circuit. The deflections obtained with various values of the capacity are plotted in Fig. 15. The dotted line shows the deflection without the condenser ($C = \text{infinity}$). The curve shows clearly a resonant value of the capacity at .45 microfarad.

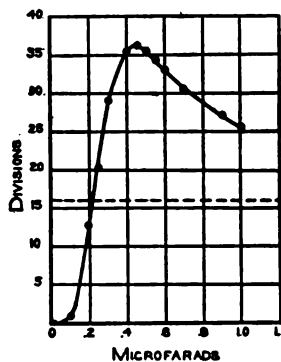


Fig. 15.

The rectifying action of carborundum is applicable in a similar manner to the study of many important problems in telephony.

I have found some other crystals that show greater sensitiveness than carborundum, when used as rectifiers of weak alternating currents. Experiments with these substances will be communicated in a subsequent paper.

Temperature Coefficient of Conductivity of Carborundum.—One of the greatest difficulties in the way of the use of carborundum in standard measuring instruments for alternating currents is the high temperature coefficient of this material. The platinized specimen No. 19 heated in an air bath gave the results shown in Fig. 16.

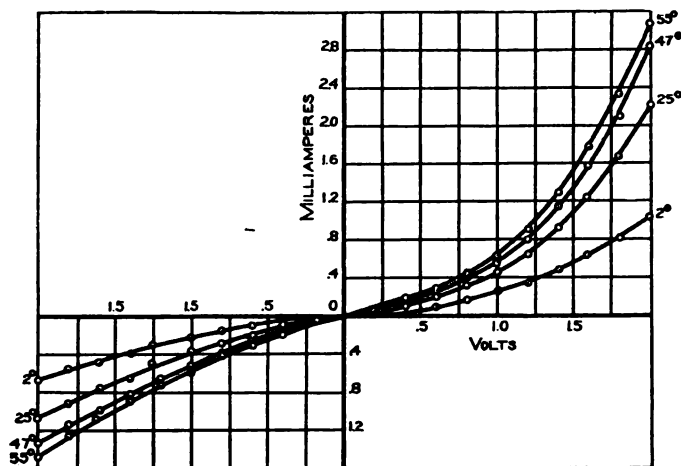


Fig. 16

Direct current was used and current-voltage curves were taken at various temperatures; namely at 2°, 25°, 47°, 55° C. By a reference to the figure it is seen that the conductivity of the substance increases with increase of temperature.

More accurate observations are shown in Fig. 17. In this case the crystal was heated in an oil bath. The electromotive force was constantly 2 volts. The curve C_1 was obtained with the current in one direction, the curve C_2 , with the current in the opposite direction. The observations were carried down below 0° C., so that any moisture present on the crystal would be frozen, and would hence be evidenced by a sudden change in the inclination of the curve.

No such change was found, indicating that the presence of free water on the crystal could not account for the unilateral conductivity. It is proposed to carry the measurements to a still lower temperature at a subsequent time in the effort to see if a temperature can be found at which the conductivity of the crystal ceases to be unilateral.

At 20° the conductivity along the curve C_1 increases 2.06 per cent. per degree, while the corresponding coefficient along C_2 is 1.52 per cent. per degree. It is interesting to note that the temperature coefficient of conductivity of neutral salts in very dilute

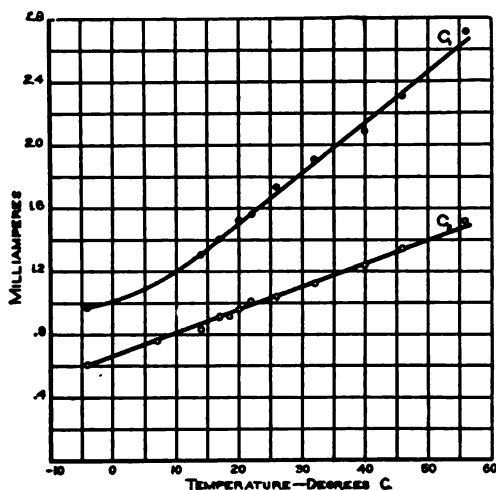


Fig. 17.

solutions is between 2.2 and 2.4 per cent. per degree, and is likewise an increase of conductivity with increase of temperature. The corresponding coefficient for copper and other pure metals is negative instead of positive and has a value in the neighborhood of .38 per cent. per degree C. It thus appears that in the matter of temperature coefficient carborundum resembles an electrolyte rather than a metallic conductor.

On the Action of Carborundum as a Detector for Electric Waves.
— The facts obtained in the above experiments contribute to an explanation of the action of carborundum as a detector for electric waves. The current-voltage curve of carborundum is not linear;

the apparent resistance of the substance drops when the current is increased, so that we might anticipate that electric oscillations through the carborundum, constituting an increase of the current, would cause a decrease of resistance and consequently a sound in the telephone, provided a local battery is used in series with the detector and telephone.

Even if the carborundum were not unilaterally conductive, this drop in resistance with increase of current would characterize the substance as a detector for electric waves as may be seen by reference to Fig. 2. For example, let us suppose that the local battery has a voltage of 2 volts, and suppose that the oscillating voltage impressed by the incident waves is $\frac{1}{2}$ volt. When this impressed E.M.F. is in the same direction as the local voltage the total voltage is 2.5, and the resulting current from the curve is 8.4 microamperes. When the impressed voltage is opposite to the local voltage, the total voltage is 1.5 volts, and the resulting current 1.8 microamperes. The average of these two current values 8.4 and 1.8 is 5.1, which is an increase of 1 microampere over the local current under 2 volts. That is to say, the average effect of a train of waves produces an increase of current in the telephone or other current operated device in series with the specimen and a local battery.

This is, however, evidently not a complete explanation of the action of the carborundum; for as General Dunwoody points out in his patent application carborundum may be used as a detector for electric waves *without a local battery in circuit*.

When employed without the local battery, the action of the carborundum as a detector is undoubtedly due to its unilateral conductivity. My experiments show that under the action of an alternating voltage more current passes in one direction than in the opposite direction. In using the detector without local battery the carborundum is shunted with a telephone, and in the case of the simplest form of receiving circuit the carborundum is in series with the antenna and ground. Electric oscillations with the voltage in one direction give a large current through the carborundum, charging the antenna. When the voltage reverses the current from the antenna to ground through the carborundum is smaller, thus leav-

ing the antenna charged with a small quantity of electricity. The effect of the whole train of waves is additive, so that this charge on the antenna is cumulative. The accumulated charge on the antenna escapes through the telephone shunted about the carborundum, causing the diaphragm to move. Each subsequent train of waves causes a similar motion of the diaphragm, which is evidenced as a note in the telephone with the train frequency of the waves.

This explanation of the action of carborundum when used as a detector for electric waves brings it into agreement in essential characteristics with a number of other detectors for electric waves, which have been comparatively studied by H. Brandes.¹ This author found that "in general, conductors or combinations of conductors which do not follow Ohm's Law are capable of acting as detectors of electric oscillations, owing to their rectifying effect. A verdict as to whether such an arrangement is more or less suitable for this purpose can be derived from the continuous-current characteristic (voltage current curve). If this characteristic be symmetrical in the first and third quadrants, such an arrangement can be used as a detector, the oscillations being superposed on a suitable continuous current. If the characteristic be asymmetric, the arrangement can be used as a detector without an external electromotive force, although a suitable auxiliary electromotive force, on which the oscillations are superposed, often increases the effect. These conclusions are arrived at as a result of considering the action of Braun's pyrolusite, Holtz's valve cell, the electrolytic detector, the Wehnelt oxycathode tube, the vacuum tube, the conductivity of flames, and Ferrie's so-called electrolytic detector without polarizing E.M.F." Among the detectors here enumerated by Brandes, pyrolusite is a crystalline solid substance of the formula MnO_2 .

The question whether or not the action of carborundum when used as a detector for electric waves is a heat effect goes back to the question whether the unilateral conductivity of the substance is of thermal origin. I am at present of the opinion that heat is practically a negligible factor in the process.

The following historical sketch of previous experiments on the

¹ *Elektrotechn. Zeitschr.*, 27, pp. 1015-1017, November 1, 1906. Quotation from *Science Abstracts*, 2078, December 28, 1906.

conductivity of crystals and allied substances is interesting in this connection.

Historical Sketch. — In 1874 Ferdinand Braun¹ in a research on the conductivity of metallic sulphides found that the current was different in different directions, and that the resistance depended on the intensity of the current. In some cases the current in one direction was as much as twice as great as the current in the opposite direction. The substances investigated were copper pyrites, iron pyrites, galena, and copper antimony sulphide. Contact was made by the use of a clamp. He says that he found no thermoelectric effect or polarization that was even remotely explicable of the phenomenon. In discussion of his results Braun puts forth a possible explanation, based on hypotheses as to the nature of the structure of the crystals.

In 1877² and 1878³ Braun returned to the subject and reported the results of further experiments, including a study of the conductivity of Psilomelan, which is a "combination of a base with manganese superoxide and water." In these experiments he showed that the pressure of the surrounding atmosphere had no effect on the phenomenon. To ascertain whether the cause of the variation of the resistance with the strength of current was due to chemical processes, he connected a copper voltameter in series with a piece of copper pyrites between silver electrodes and a piece of Psilomelan between gold electrodes. After the current from eight Grove cells had been running for nine hours, he found that the current had separated out 1.404 grams of metallic copper in the voltameter while the silver electrodes in contact with the pyrites showed no trace of silver sulphide. Also the pyrites and Psilomelan showed no appreciable decrease in weight. As further evidence that there was no electrolysis of the substances, Braun found that two electrodes of different metals at the same temperature when placed in contact with the mineral gave no current.

Another important result obtained by Braun is the fact that when a constant current is sent through the body simultaneously with an induced current from an induction coil, the resistance is lowered, not only for the former but also for the latter.

¹ Pogg. Ann., 153, p. 556, 1874.

² W. A., 1, p. 95, 1877.

³ W. A., 4, p. 476, 1878.

This work of Braun was considerably discussed at the time by writers who were unable to obtain the phenomenon or who advanced the opinion that the effects were of thermoelectric or electrolytic origin. In his papers of 1877 and 1878 and in 1883¹ Braun replied to these objections, and maintained that thermoelectric processes and electrolytic polarization could not account for the phenomenon.

In 1900 and 1902 in the course of a research on the electric conductivity of compressed powders, F. Streintz² investigated among other things a great many oxides and sulphides of metals. None of the substances examined (in the form of finely divided powder) "showed electrolytic conductivity." Streintz also determined the temperature coefficients of conductivity, and found that compounds that at ordinary temperature conduct well have positive temperature coefficients of resistance, less, however, than the coefficients of pure metals. Compounds, on the other hand, whose conductivity at ordinary temperature is relatively small were greatly influenced by temperature, their conductivity increasing with increase of temperature. In this latter class belong PbS , HgS , Ag_2S , and MnO_2 . A very remarkable change of conductivity with temperature was obtained with Ag_2S , as has been previously noticed by Faraday³ and Hittorf.⁴

On the question of the thermoelectromotive force of metallic couples a very interesting series of results have been obtained by A. Abt⁵ in a research entitled "Thermoelectromotive Force of Some Metal Oxides and Metal Sulphides in Combination with One Another and with Simple Metals with 100° Difference of Temperature of the Contact Points." According to these experiments oxides and sulphides of metals arrange themselves in the following thermoelectric series :

Chalcopyrites	Copper	Iron
Pyrolusite	Cadmium	Pyrrhotite
Bismuth	"Nickelerz"	Antimony
Zinc	Arc Light Carbon	Pyrite
Nickel.		

Relative to the couple bismuth-antimony considered as unity the chalcopyrite-pyrite couple has a thermoelectromotive force of 10.8.

¹ Wied. Ann., 19, p. 340, 1883.

² Ann. d. Phys., 3, p. 1, 1900; also 9, p. 854, 1902.

³ Faraday, Pogg. Ann., 31, p. 241, 1834.

⁴ Hittorf, Pogg. Ann., 84, p. 20, 1851.

⁵ Abt, Ann. d. Phys., 2, p. 266, 1900.

From this work it is evident that the thermoelectric effects with crystals may be large in comparison with metallic couples, and this fact must be taken into account in dealing with the unilateral conductivity of crystalline substances.

SUMMARY OF RESULTS.

1. Current voltage curves for carborundum are shown.
2. Carborundum is unilaterally conductive. With one specimen under 10 volts the current in one direction is 100 times the current in the opposite direction. With another specimen platinized on one side the current at 34.5 volts is 527 times as great as the current in the opposite direction under the same voltage. In another case at 30 volts the current in one direction is 4,000 times the current in the opposite direction under the same voltage.
3. As the current increases the efficiency of rectification decreases.
4. A specimen platinized on both sides has a smaller efficiency of rectification and a much lower resistance than a piece not platinized. Though the efficiency of rectification is less with the platinized specimen, the *excess* of one current over the other for a given voltage is much greater with the platinized specimen on account of its low resistance.
5. An oscillogram is given showing the distortion of an alternating current wave by carborundum.
6. A method is shown of employing crystal rectifiers in the construction of alternating current measuring instruments.
7. These instruments are applicable to the measurement of telephonic currents, and may be used in experiments on resonance in telephone circuits.
8. A determination of the temperature coefficient of conductivity of carborundum is given. This coefficient is in the neighborhood of the temperature coefficient of weak electrolytes.
9. A discussion is given of the action of carborundum in General Dunwoody's detector for electric waves.
10. No theory is given as to the cause of the unilateral conductivity of carborundum. A number of other crystals have the same property, and it is proposed to accumulate data in regard to these other substances before attempting an explanation.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY, CAMBRIDGE, MASS.,
May 6, 1907.

THEORY OF CONTROL OF THE ALTERNATING
CURRENT GALVANOMETER.

BY A. H. TAYLOR.

THE instrument to be discussed in this paper is really a shunt circuit dynamometer with a laminated iron field. Or, it is an ordinary D'Arsonval having a laminated iron field separately excited by a current drawn from the same source as the alternating current to be detected.

Since the moving coil hangs in an alternating field, it must either not be wound on a copper frame, or else the reaction of the frame (due to eddy currents) must be compensated for after the manner of Stroud and Oates,¹ who used this method of controlling the initial equilibrium position of the moving coil. A more satisfactory method of control is the one devised by Terry;² a method which allows equally flexible control on a great variety of external circuits.

Providing that the suspensions are not too heavy, they have in general but little to do with the initial position of the coil when the field current is on, since the induced currents in the coil react with the field in such a way as to produce a torque whose direction depends on whether the induced current leads or lags with respect to the induced E.M.F. Reference to Fig. 1 will explain this. Let AA be a fixed line, while OF is a rotating vector whose projections on AA give the instantaneous values of the field. This alternating field will induce in the coil the E.M.F. represented by the rotating vector OE . Since the coil has a large inductance (80 millihenries), the induced current will generally lag, and may be represented by the vector OC . But if the outside circuit contain sufficient capacity (in series or in shunt) the induced current may lead the E.M.F., and hence must be represented by the vector OC' . Since the torque will be proportional to the product of field and induced current, it is evident that the torque due to OF and OC

¹ Stroud and Oates, *Phil. Mag.*, Dec., 1903.

² Terry, *PHYS. REV.*, Sept., 1905.

will be opposite in direction to that due to OF and OC' , while if there is no lag or lead, there will be no torque except that of the suspension.

The fact that the projections of OF and of OC during the greater part of the cycle have opposite algebraic signs, means that the relation shown in Fig. 2 holds for most of the cycle. N and S repre-

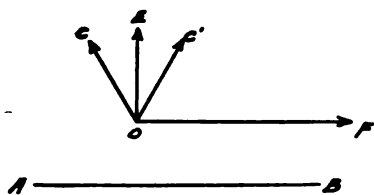


Fig. 1.

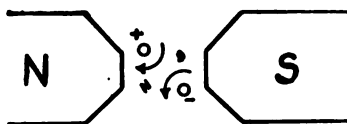


Fig. 2.

sent the instantaneous polarity of the pole pieces of the field; n and s represent the instantaneous polarity of the coil faces.

The reaction will evidently be such as to hold the coil in a position of stable equilibrium with its plane parallel to the field.

The direction of torque may be determined analytically as follows: Let the magnetic field be $f = F \sin \omega t$, where F is the maximum value. The induced E.M.F. is

$$E = -\frac{dn}{dt} = -K \cdot \frac{df}{dt}$$

where K is a constant depending on the geometry of the coil, and the angle its plane makes with the field. The induced E.M.F. may be written $e = -E \cos \omega t$ where E is the maximum value. If Z is the impedance of coil and circuit, the induced current is

$$i = -\frac{E}{Z} \cos (\omega t + \varphi) = -I \cos (\omega t + \varphi)$$

when I is the maximum value, and φ is the phase angle. The torque is

$$T = \int_{2\pi/\omega}^0 i f C \cdot dt = \frac{CFI}{2} (\cdot \sin \varphi)$$

where C is a constant depending on the magnetic moment of the coil. If the induced current lags, φ is negative and $\sin \varphi$ is also negative. Hence the torque is negative. If the induced current leads, φ is positive, and hence the torque also is positive.

To use the galvanometer as a detector of alternating current, it must be permanently connected to the circuit. If the coil is too stable in the first position, with its plane parallel to the field, it must be shunted with a capacity whose effect may be regulated by a resistance in series with the same ; if the coil turns its plane perpendicular to the field, it must be shunted with a resistance. Hence, on any but a very low resistance external circuit, the control circuit may be regulated very easily so that the coil is not constrained by its own induced currents. Then the current to be detected is applied to the external circuit, and produces its effect as in any galvanometer.

A current cannot be *measured* unless the relative phase angle between current and field be known, but for bridge work the instrument is extremely useful, being fully as sensitive as any instrument for the detection of alternating currents, and possessing the great advantage of being applicable to commercial circuits of ragged wave-form and inconstant frequency. It is not possible to obtain a current through the coil 90° out of phase with the field under any ordinary conditions of bridge work ; if it were momentarily possible, it could last for only a very short time on account of the variations in frequency of the average commercial circuit. Hence there will, in general, always be a deflection when a current passes through the coil.

This galvanometer has been used for precise A.C. bridge work in this laboratory for three years, giving excellent results in the hands of students, and as many inquiries concerning it have come to me from those compelled to use commercial circuits for A.C. precision work, I am taking this opportunity of pointing out its merits and demerits.

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THE EXTRA-TRANSMISSION OF ELECTRIC WAVES.

BY W. B. CARTMEL.

LAST Christmas I presented at the New York meeting of the American Association for the Advancement of Science a paper, having for its title "The Optical Analogue of Certain Electrical Experiments." In it I tried to account for a phenomenon observed by Messrs. Blake and Fountain,¹ and mentioned in a paper they have recently published, in an entirely different way from what they did. Since then a paper by Mr. Schaefer² has appeared, in which he tries to show that it is unlikely that the phenomenon exists at all. For this reason I have undertaken in the present paper to discuss the experiments of Blake and Fountain from a somewhat different standpoint than theirs. It seems to me that the results obtained by these two experimenters are not only not unreasonable, but they are precisely what one ought to have expected.

In their experiments Blake and Fountain allowed electric waves to fall upon sheets of glass upon which tin-foil strips had been pasted, and also upon sheets of bare glass, and found that when the tin-foil covered sheets of glass were used, under some circumstances there was less energy reflected, and more transmitted than was the case with bare glass. This they account for by assuming that glass covered with tin-foil strips constitutes a medium having a different index of refraction than that of glass. To me it seems more plausible to suppose that since the total energy reflected by bare glass is the vector sum of the amounts reflected by the front and back surfaces of the glass, and since the change of phase produced at a surface on which there are tin-foil strips is different from that produced at a bare glass surface, it might well happen that the tin-foil strips would cause the difference of phase between the energy reflected at the two surfaces to be more favorable to destructive in-

¹F. C. Blake and C. R. Fountain, *PHYS. REV.*, XXIII., p. 257, 1906.

²C. Schaefer, *PHYS. REV.*, XXIV., p. 421, 1907.

terference, and that there would be a consequent diminution in the reflected intensity and an increase in the transmitted. That such a change of phase is produced by screens of resonators is more than likely, especially in view of the fact that gratings produce a change of phase, as has recently been shown experimentally by Messrs. Schaefer and Laugwitz.¹

If the above explanation of the phenomenon of extra-transmission be correct, it ought to be possible to obtain the same effect with ordinary light. All that is necessary is a sufficiently thin film of one substance and upon this a very much thinner film of some other substance, to produce the necessary phase change. Now the phase change produced at the surface of a transparent substance is either zero or π while that produced by sufficiently opaque substances like the metals or certain dyes is different from either zero or π . The phase change produced by a thin film of metal depends upon its thickness as well as upon the optical contents of the metal. As the thickness of a thin film of metal diminishes the change of phase and the intensity of the reflected light will both diminish, but while with diminishing thickness the intensity approaches zero as its limit, the change of phase approaches a certain finite constant value, which is practically the same for all thicknesses less than one thousandth of a wave-length. This value is in the case of silver and gold about six tenths of the value of the phase change produced by thick plates, as has been shown by G. T. Walker² and by Maclaurin.³ One ought therefore to be able to realize this effect of extra-transmission by taking a film of some substance thin enough to show interference colors, and depositing upon it a mere suspicion of silver. This coating of silver would produce the necessary phase change, while being perfectly transparent. I tried to obtain the effect by silvering pieces of blown glass which showed interference colors, but did not meet with much success. This was no doubt due to the low reflectivity of the glass which is only about 4 per cent. With substances like selenium or the aniline dyes whose reflectivity is as high as 25 per cent. or 30 per cent. for some colors, one might

¹ C. Schaefer and M. Laugwitz, *Ann. der Physik.*, XXI., p. 587, 1906.

² G. T. Walker, *Ann. der Physik*, X., p. 194, 1903.

³ R. C. Maclaurin, *Proc. Roy. Soc.*, 1906. Series A, Vol. LXXVIII, p. 302.

obtain much more noticeable effects. I therefore silvered lightly a film of selenium which had been deposited on glass by cathode discharge. The result was that the film of selenium which was previously of an orange color, changed to purple. This would show that there was less purple light reflected after silvering and hence more transmitted. The film of silver was very thin — it had only required fifteen seconds to deposit it by cathode discharge — and where it fell on bare glass it was impossible to detect it by the eye. Part of the plate had been protected from cathode discharge, and the only way in which it was possible to tell where the silver had fallen was by the difference in color of the two parts of the selenium film. In another case a film of selenium too thin to show interference colors was deposited upon a glass plate and this gave the glass a light brown color. Upon part of it an extremely thin coating of silver was deposited. By transmitted light the unsilvered part appeared darker than the silvered.

Experiments were also tried with compound films of fuchsine and silver. Half of one side of a glass plate was lightly silvered with the intention of afterwards depositing fuchsine upon it. I was unable to tell which side was silvered try as I might, but I thought I remembered that I had exposed to cathode discharge the side of the glass plate which was least scratched, and so proceeded to deposit from an alcoholic solution a film of dye upon what was thought to be the silvered side. The dye showed plainly that this side had been silvered, because where the dye film crossed the silver film, it was plainly more transparent than it was where it covered bare glass. The increase in transparency was still more marked when the silver was deposited on the fuchsine instead of being between the fuchsine and the glass. Indeed a thin wash of fuchsine on glass vanished from sight almost entirely by being silvered. This I do not believe to have been due to an annihilation of the dye caused by the bombardment by the silver cathode particles because the dye reappeared when the plate was washed with alcohol: that is to say, the alcohol became colored with the dye that was on the plate.

In the discussion of my paper at the meeting of the American Association, it was suggested that possibly the films had been

chemically acted upon by the silver so as to produce a change of color or an increase of transparency. That this was not so in the case of selenium at least, was proved by a wedge shaped deposit of selenium, which showed interference colors, something like Newton's rings. On lightly silvering a part of this the interference bands of the silvered part were displaced relatively to those of the unsilvered part.

Let us now return to the experiments of Blake and Fountain. They allowed not light, but electric waves of wave-length 9.9 cm. to fall on glass plates about a meter square. One of the plates was 5 mm. thick and the others were 3 mm. thick. They found that the thick plate reflected 38 per cent. and transmitted 60 per cent. of the incident radiation, while those of 3 mm. thickness reflected 17 per cent. and transmitted 80 per cent. The fact that the sum of the reflected and transmitted radiation is nearly unity in both cases, is a very good check on the work. Furthermore, from their data we can compute the index of refraction of the glass by Airy's formula.

$$I = \frac{4a^2b^2 \sin^2 \frac{1}{2}\delta}{(1 - b^2)^2 + 4b^2 \sin^2 \frac{1}{2}\delta}$$

in which a^2 is the intensity of the incident radiation; b^2 is the reflection coefficient, which is connected with the index of refraction as follows:

$$b^2 = \left(\frac{n - 1}{n + 1} \right)^2.$$

$$\delta = \frac{4\pi n e \cos r}{\lambda},$$

e is the thickness of the plate, λ the wave-length in air, and r the angle of refraction.

Using these formulæ one gets the same value for the index of refraction of the thin pieces and the thick piece of glass, viz.: 2.41, which would make the dielectric constant about 5.8. These results are evident from the curves shown in Figs. 8 and 9¹ of their paper.

In the curve of Fig. 8, one may notice that the addition of the resonators causes the reflected intensity to increase. This increase

¹ Ibid., p. 269.

becomes greater as the resonators are made longer, until a resonator length of 2.7 cm. is reached after which increasing the resonator length diminishes the reflected intensity. This is not because the energy reflected at the tin-foil covered surface is a maximum for a resonator length of 2.7 cm., but because the vector sum of the energy of the rays from the front and back surfaces of the plate is a maximum at this point. If the glass had been left bare and the phase relations between the rays from the front and back surfaces had been changed by varying the thickness of the plate, the maximum of the reflected intensity would have occurred at a thickness

$$e = \frac{\lambda}{2\pi n \cos r} = .65 \text{ cm.}$$

and this maximum would not have been greater than about 49 per cent. With the resonators on the plate the maximum reflected intensity was 53 per cent., which goes to show that the resonators increased the reflectivity of the surface upon which they were pasted, as well as changing the phase of the reflected energy, and the figure also shows that they introduced some real absorption, as might have been expected.

In Fig. 8 one sees that the intensity of the reflected energy never reaches the highest possible value, but attains its maximum at a resonator length of 3 cm. where the phase change is a maximum. The intensity having its maximum at the same point as the maximum phase change, causes the curve to be rather symmetrical about a center line, which is not the case in Fig. 9.

All of the foregoing considerations, it seems to me, tend to make the results published by Blake and Fountain very plausible, though I do not think this kind of reasoning should be pushed too far. There are other effects coming in due to the fact that the thickness of the glass is of the same order of magnitude as the resonator widths and lengths. The different absorptions as shown by the dotted lines of Figs. 8 and 9, and no doubt the phase changes, are also affected to some extent by the nearness of the second surface of the glass. If, however, Mr. Schaefer had only given in his paper the results which he obtained when he tried to verify Blake and Fountain's experiments, his evidence would have had more weight.

We do not know whether his glass was thick or thin, whether it had a high or low index of refraction, nor what the reflection and transmission of the bare glass was. From his curves of reflection and transmission for different lengths of resonators, together with the same data for bare glass, it ought to be possible to decide whether or not an increased transmission should be expected in his case. In obtaining an increased transmission of light through thin films by silvering them, I had no success for a long while, because I silvered the films a little too much, so that what was gained by phase change, was lost by the absorption of the silver film. Some such thing may have prevented Mr. Schaefer from obtaining increased transmission, or it may be that the index of refraction of the glass plates that he used was too low. The index of refraction of the glass Blake and Fountain used was high — the reflection coefficient was 17.1 per cent. — while some glass is known to have a very low dielectric constant, and no doubt has a correspondingly low reflection coefficient. If the dielectric constant of Mr. Schaefer's glass was 3, a by no means improbable value, the index of refraction would probably be 1.73 and this would give 7.2 per cent. for the reflection coefficient. It is evident that with such a low reflectivity the effect of extra-transmission would be difficult to observe.

Finally I wish to say that I am not in a position to judge as to the reasonableness of the criticisms Mr. Schaefer makes of the adjustments of Blake and Fountain's apparatus. Their results seem to be good. Even if Mr. Schaefer can show that Blake and Fountain's results are wrong, which I doubt very much, it ought still to be possible for some one to obtain a true extra-transmission.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
May 27, 1907.

PROCEEDINGS
OF THE
AMERICAN PHYSICAL SOCIETY.

THE RELATION BETWEEN LUMINOSITY AND ELECTRICAL
CONDUCTIVITY OF FLAMES.¹

BY F. L. TUFTS.

THE paper was in part a reply to an article by C. Fredenhagen (*Annalen der Physik*, Band 20, Heft 1, 1906, p. 151) in which he calls in question a conclusion of the author in an earlier paper (*Physikalische Zeitschrift*, 5 Jahrgang, No. 6, p. 157), to the effect that the electrical conductivity imparted to the bunsen flame by the salts of sodium and lithium respectively varied directly as the luminosity of the yellow sodium line or the red lithium line.

The author pointed out that in the experiments by Fredenhagen the real quantities compared were the resistances at the surface of his cathode and not the conductivities of the flame gases between his electrodes. By means of data already published (*PHYSICAL REVIEW*, Vol. XXII., No. 4, April, 1906, p. 193) and some recent experiments by the author it was shown that in the case of the red lithium line and the yellow sodium line the luminosity varies directly as the electrical conductivity imparted to the flame by the salt vapors, whether the variation is produced by varying the rate of supply of air, gas, or salt spray to the flame, or by the introduction into the flame of chlorine gas or chloroform vapors. A discussion of these results led to the conclusion that both the luminosity and the ionization imparted to the bunsen flame by the salts of lithium and sodium were directly connected with the formation in the flame of the oxides of these metals.

Some experiments were also described on the effect of adding chlorine gas to the pure bunsen flame, and it was shown that while the addition of the gas caused a marked decrease in the electrical conductivity of the flame, it produced an increase in the luminosity of the Swan spectrum. It is evident in this case that the reactions to which the Swan spectrum luminosity is due are productive of little if any of the flame conductivity while the reactions producing the flame ions are not productive of much luminosity.

¹ Abstract of a paper presented at the New York meeting of the Physical Society, March 2, 1907.

THE EFFECT OF FREQUENCY UPON THE CAPACITY OF ABSOLUTE CONDENSERS.¹

BY J. G. COFFIN.

IT has been proposed to construct an absolute condenser of two plates of optically plane glass. In order to render the faces conducting and at the same time employ the well known method of Perot and Fabry for determining their parallelism and their distance apart, it is necessary to half-silver the opposing faces of these plates. If such a condenser is to be charged and discharged many times a second as is usually the case in their comparison with others, a doubt arises as to the completeness with which they acquire their charges, in view of the inevitable fact that this conducting film has a very high resistance. A theoretical calculation was made of this effect with rather surprising results: for example if the condenser be two plates of rectangular shape 10 cm. long, resistance of 5000 ohms per lin. cm. and capacity of 100 cm. per lin. cm., it was found that at a frequency of 1000 alternations per sec. the ordinarily assumed capacity was 1 per cent. too large, while if the frequency rose to 10000 per sec. it was 65 per cent. too large.

The mathematical method employed is one involving the imaginary variable, and is somewhat similar to the method used in calculations of the influence of frequency upon the self-inductance of coils, with which the writer has had a great deal to do lately.

The two additional cases of a circular plate condenser, involving Bessel's functions, and that of a circular ring condenser involving ordinary functions, have also been solved. The results are in agreement with those for the rectangular condenser mentioned above.

In conclusion it is found that condensers with plates of high resistance when used with alternating currents cannot be assumed to have their maximum capacity as ordinarily calculated. Their effective capacity decreases with increasing frequency and this diminution may attain large values even under moderate frequencies.

ON THE VARIATIONS OF RESISTANCES WITH ATMOSPHERIC HUMIDITY.²

BY E. B. ROSA AND H. D. BABCOCK.

IN the course of an extended investigation on the ratio of the electromagnetic to the electrostatic units³ it was found that all the resist-

¹ Abstract of a paper presented at the New York meeting of the Physical Society, March 2, 1907.

² Abstract of a paper presented at the Washington meeting of the Physical Society, April 1-20, 1907.

³ By Rosa and Dorsey.

ances employed had a higher value at the same temperature in summer than in winter, the change being a gradual drift upward from early spring to midsummer, followed by a steady drift back to the same minimum in the winter. The amplitude of the change was of course small, varying from 15 to 25 parts in 100,000, but far too large to be neglected in precision work.

The possibility of this change being due to atmospheric humidity suggested itself, but it was not at first evident how an increase of resistance could be produced by an increase of humidity. The effect of leakage arising from moisture deposited on the coils is of course to decrease the resistance, and this effect would increase with the humidity. In order to ascertain the cause of the marked change in the opposite direction, to determine its magnitude and to find how to prevent it we took up last November a systematic study of the question.

It was very soon found that changes such as occurred during an interval of six months in the atmosphere of the laboratory could be induced in a few days by placing the resistances in a closed case in which an atmosphere of high humidity was maintained. Two such cases were employed, one being kept at a constant relative humidity of about 25 per cent., the other at higher humidities, ranging from 40 to 100 per cent., although seldom higher than 80 per cent., and usually about 60 per cent. Each case was provided with thermometers and recording hydrometers.

The resistances were measured generally to one or two parts in a million, always to within a few parts in a million, and corrections made for the small fluctuations in temperature. All measurements were referred ultimately to the standard one-ohm coils of the bureau, the change of resistance of which due to this cause is known to be very slight.

The following are some of the most important results so far obtained :

1. Shellacked coils of manganin wire, such as those contained in the Richsanstalt form of standards, and in potentiometers, wheatstone bridges and various forms of resistance boxes (as made by many different makers) increase in resistance as the humidity increases, and slowly come to a final value at any given humidity.
2. They gradually return to the original values when the humidity is reduced to its original point and maintained constant.
3. The change is greater on coils wound with fine wire, such as 1,000 and 10,000 ohm coils than with coils of 10 and 100 ohms. It is very slight or inappreciable on coils of 1 ohm and less.
4. Such coils of 1,000 ohms wound on metal spools change by as much as several hundred parts in a million when transferred from a dry atmosphere to one of 80 per cent. humidity.
5. Similar coils on wooden spools, the latter having been thoroughly coated with shellac as well as the wire and then baked, change sometimes five or ten times as much as the coils on metal spools.

6. Coils having a heavy coating of shellac may change more than those covered by a light coating.

7. Shellacked coils whether on metal or wood spools, remain constant in value when sealed airtight.

8. Shellacked coils submerged in oil change with change of humidity, but more slowly and to a less extent.

9. Calcium chloride placed in the bottom of the box of resistances keeps the air in the box more nearly at constant humidity, and so reduces the fluctuations of resistance, but will not keep the resistances constant unless the box is airtight.

10. In a saturated or very humid atmosphere the resistance may decrease and become unsteady due to leakage from moisture deposited on the coils. But this does not occur until after the resistance has gone up considerably, and seldom occurs except in a saturated atmosphere.

11. Coils that are covered by paraffine, whether they have been previously coated with shellac and baked or not, do not change in resistance as the humidity is increased. This is true whether the coils are on metal or wood spools, provided in the latter case the wood spool has been filled with paraffine.

12. The cause of the increase of resistance appears to be the stretching of the wire due to the shellac expanding as it absorbs moisture. On drying out in a dryer atmosphere the shellac and the wire embedded in it contract to their original volume and the resistance falls to its original value.

13. That shellacked coils kept submerged in pure oil change slowly with the humidity indicates that an appreciable quantity of moisture is absorbed by the oil and so gets into the shellac.

14. Paraffine does not absorb moisture and hence protects the shellac from atmospheric moisture when the shellacked coil has been dipped in hot paraffine.

15. Coils on wood spools change in resistance more than coils on metal spools because the shellacked wood spool, as well as the shellac in which the wire is embedded, expands by absorption of moisture.

16. Shellacked coils kept in air and submerged in oil for measurement show the same changes as when measured in air. The moisture in the shellac which has caused the shellac to swell and stretch the wire, comes out very slowly into the oil. If the spool is dry, it may gain moisture from the oil (see 13).

17. Sterling varnish absorbs moisture and expands, causing the resistance to increase, but not as much as shellac.

18. Shellacked coils that have been kept in a relatively dry atmosphere of 25 per cent. of humidity lose moisture and decrease in resistance when placed in a closed space with phosphorus pentoxide.

19. Metal spools covered with dry silk and wound with dry silk-covered wire absorb enough moisture in a humid atmosphere to appreciably increase their resistance.

20. Shellacked coils that have been baked increase in resistance after cooling (1) by reason of the aging of the wire, and (2) by absorption of moisture from the air.

21. The decrease in resistance of a shellacked coil due to temporary or accidental heating is partly due to the driving off of moisture by the heat.

22. High resistances of manganin coated with paraffine or sealed in an airtight space are remarkably constant in value, apparently as constant as low resistances.

23. Old resistance boxes containing manganin coils coated with paraffine show no changes due to humidity, and may even be plunged in water without appreciable changes of resistance. This shows that the paraffine does not absorb moisture and is not cracked appreciably by age.

24. Shellacked coils submerged in water absorb moisture so fast as to become polarized, and their resistance decreases rapidly instead of increasing as in a moist atmosphere.

A new form of sealed resistance standards are being developed.

BUREAU OF STANDARDS,
WASHINGTON, April 15, 1907.

THE SIMULTANEOUS MEASUREMENT OF THE CAPACITY AND POWER FACTOR OF CONDENSERS.¹

BY FREDERICK W. GROVER.

IN a condenser having absorption, the angle of advance between the current and the electromotive force is less than 90° by a small angle θ , the power factor being equal to $\sin \theta$. A condenser having absorption is equivalent, therefore, in its effect on the phase of the current, to a capacity in series with a small resistance r of such a value that $\tan \theta = pCr$ (where $p = 2\pi$ times the frequency) or to a capacity in parallel with a large resistance R such that $\tan \theta = 1/pCR$.

The power factor of a condenser is more accurately measured by determining this small angle θ than by direct measurement of the energy loss itself. Such measurements of the phase difference have been made by Potts² using one of Rowland's electro-dynamometer methods, and by Rosa,³ who has developed a number of dynamometer methods, and shown that they give results in good agreement with one another, and with his results on the same condensers by a calorimetric method.⁴

¹ Abstract of a paper presented at the Washington meeting of the Physical Society, April 19-20, 1907.

² Amer. J. Sci. (4), 10, p. 91, 1900; Phys. Zs., 2, p. 301, 1901.

³ Bulletin of Bureau of Standards, 1, p. 383, 1905.

⁴ Rosa, PHYS. REV., Feb., 1899.

In 1891 Max Wien¹ gave several alternating current bridge methods for the measurement of inductances and capacities. Among these is one where the absorption of the condenser to be tested, which he represented by a resistance in parallel with a capacity, is compensated for by an adjustable resistance in series with the standard capacity. The absorption of the latter is assumed to be zero. An elaborate investigation of the energy losses in the dielectric of cables has been published, since the work in this paper was begun by Monacsh,² in which Wien's method was successfully used.

The following three bridge methods have been found satisfactory. In the first three, each side of the bridge consists as usual of a capacity in series with one of the ratio coils. The phases of the currents in the two sides of the bridge are brought into unison,

1. By an adjustable resistance in series with the standard condenser.
2. By an adjustable resistance in parallel with the standard condenser.
3. By a variable inductance in series with that ratio arm which is adjacent to the condenser to be tested.

Method I. — This is the same in principle as that of Wien described above, except that, whereas he derived the formula on the assumption that the resistance representing the absorption was in parallel with the condenser, the author has adopted the assumption that it is in series with the condenser. Physically it is, of course, immaterial which assumption is adopted, since we are only concerned with the change in the phase of the current due to the presence of the absorption.

It is more convenient in practice to introduce a series resistance ρ into each condenser arm. Then

$$\frac{C_1}{C_2} = \frac{R_2}{R_1}$$

$$\tan(\theta_1 - \theta_2) = \rho C_2 \rho_2 - \rho C_1 \rho_1.$$

Method II. — To avoid the necessity of working with resistances of several megohms it is best to put a resistance ρ in parallel with each of the condensers. Then

$$\frac{C_1}{C_2} = \frac{R_2}{R_1}$$

$$\tan(\theta_1 - \theta_2) = \frac{1}{\rho C_2 \rho_2} - \frac{1}{\rho C_1 \rho_1}.$$

This method is not so good as the other two, since the sensible electrostatic capacities, inseparable from such large resistances, must be added to the capacities of the condensers. The power factor measurement is not, however, affected by these capacities.

¹ Wied. Annalen, 44, p. 681, 1891.

² Inaugural Dissertation, Dantzig, 1906.

Method III. — In practice a fixed inductance L_2 is inserted in one arm and a variable inductance L_1 in the other. Then

$$\frac{C_2}{C_1} = \frac{R_1}{R_2}$$

$$\tan (\theta_1 - \theta_2) = \frac{\rho L_1}{R_1} - \frac{\rho L_2}{R_2}.$$

This method has the advantage that nothing is placed in the arms with the condensers. It is, therefore, especially adapted to the comparison of capacities as small as 0.001 mf., where in Method I. the errors due to capacity of the large resistances r , required with such small capacities, may become appreciable.

To obtain the most precise results with these three methods, the condensers should be nearly equal in capacity and power-factor, and it is best to balance each of the two capacities against that of a third auxiliary condenser. This procedure has the following advantages:

1. Errors due to electrostatic induction between the bridge and its surroundings are practically eliminated.

2. The ratio of the two capacities is proportional to the two nearly equal settings of the same resistance box, making an accurate determination of the actual values of the coils unnecessary.

The following method has been found satisfactory and is especially valuable as a check on those already given, since it is very different in principle.

Method IV. — It has been shown¹ that in the comparison of an inductance with a capacity by Anderson's method, the effect of the absorption of the condenser on the value of the inductance obtained is in all ordinary cases extremely small. The difference in the actual value of the resistance Q' of the arm containing the inductance from the value Q with direct current, due to the absorption of the condenser, may become very appreciable.

$$Q' = Q + \rho L \tan \theta$$

$$\therefore \tan \theta = \frac{Q' - Q}{\rho L} \quad (A)$$

If settings be made with first one condenser, and then with the other

$$\tan (\theta_1 - \theta_2) = \frac{\Delta Q'}{\rho L}$$

where $\Delta Q'$ is the difference between the values of Q' in the two cases, and

¹ Rosa and Grover, Bulletin of Bureau of Standards, 1, p. 312, 1905.

$$\frac{C_1}{C_2} = \frac{2r_2 + P}{2r_1 + P}$$

if the ratio arms P and R are equal.

This is inherently a substitution method, and by properly choosing Z so as to give a satisfactorily large value to ΔQ , good results have been obtained.

The absolute values of the power factor of a condenser follows at once from measurements with these methods, if some standard of reference is at hand. For capacities of 0.1 mf. and smaller, comparisons were made directly with air condensers of negligible leakage. The values for the larger capacities were obtained by stepping up from 0.1 mf., using the relation that the resultant power factor f of the two condensers of capacities C_1 and C_2 and of power factors f_1 and f_2 is given by

$$f = \frac{C_1 f_1 + C_2 f_2}{C_1 + C_2}$$

As a check on this process, the power factor of a 1 mf. condenser was determined by using a formula (A) of Method IV., the observed value of $(Q' - Q)$ being corrected for the effect of the known residual inductances and capacities of the arms of the bridge. The result agreed closely with that given by stepping up from the 0.1 mf. air condenser. Care must be taken in using formula (A) that the change in resistance of the coil Z with the frequency is negligible, otherwise it must be determined and allowed for.

RESULTS.

These four methods have been tested by measurements on a large number of condensers, at frequencies between 30 and 1,000 cycles (using vibration galvanometers to balance the bridge). The capacity ratios obtained by the different methods agree to a few parts in 100,000, while the differences $(\theta_1 - \theta_2)$ do not differ more than can be explained by the errors in the setting of the bridge. It has been found:

1. For good mica condensers the angles θ may be as small as 0' 30" and as large as 4'. Poorer mica condensers, especially if their capacity is small may give values of θ as large as 30' or even more.
2. Good condensers with paraffined paper for a dielectric have a value of from 5' to 20'; for poor telephone condensers angles as large as 10° have been observed!
3. For all the mica condensers examined the angle θ diminishes slowly as the frequency rises.
4. The same result was observed with all the poorer paper condensers, but with some of the better paper condensers the effect was in the opposite direction. The changes are all greater than in the case of mica condensers.

5. Above 20° the power factor increases with rise of temperature both in mica and in paper condensers, the effect being small for the former and very large for some of the poorer paper condensers.

Since the power factor depends primarily on the absorption, the leakage having but a small effect, the value of the power factor would be expected to give a relative indication of the magnitude of those effects which depend on absorption, viz: residual charges, change of capacity with the frequency, dependence of the apparent capacity on the time of charge and discharge, etc. Ballistic measurements show that this hypothesis is substantiated qualitatively and, approximately, quantitatively. A measurement of the power factor gives, therefore, valuable information as to the quality of the condenser.

These effects of changes of frequency and temperature are being more thoroughly investigated.

AN EXACT FORMULA FOR THE MUTUAL INDUCTANCE OF COAXIAL SOLENOIDS.¹

BY LOUIS COHEN.

VARIOUS approximate formulas have been given for the calculation of the mutual inductance of solenoids, some of them give results to a higher degree of approximation than others, but in every case the degree of approximation will depend on the dimensions of the solenoids.

In many cases it is absolutely important to know to what degree of approximation we can calculate the mutual inductance by any given formula, and for this reason it is very desirable to have an exact formula by means of which we can determine the degree of approximation of the various approximate formulas.

The exact formula obtained in this paper was derived in the following manner: We start with Neumann's expression for the mutual inductance of two coaxial circular currents.

$$M_1 = \int_0^{2\pi} \int_0^{2\pi} \frac{\cos \epsilon ds ds_1}{r},$$

and then integrate over the lengths of both solenoids we get

$$M = \int_0^l \int_0^{l_1} M_1 dx dx_1 = \int_0^l \int_0^{l_1} \int_0^{2\pi} \int_0^{2\pi} \frac{\cos \epsilon ds ds_1 dx dx_1}{r}.$$

The value obtained for M is as follows:

$$M = 4\pi n n_1 (V - V_1),$$

where

¹ Abstract of a paper presented at the Washington meeting of the Physical Society, April 19-20, 1907.

$$\begin{aligned}
 V = & -(A^2 - a^2)c \left[F\left(k, \frac{\pi}{2}\right) \{F(k', \theta) - E(k', \theta)\} - E\left(k, \frac{\pi}{2}\right) F(k', \theta) \right. \\
 & + \frac{c^4 - (A^2 - 6Aa + a^2)c^2 - 2(A^2 - a^2)}{3\sqrt{(A+a)^2 + c^2}} F\left(k, \frac{\pi}{2}\right) \\
 & \left. + \frac{2(A^2 + a^2) - c^2}{3} \sqrt{(A+a)^2 + c^2} E\left(k, \frac{\pi}{2}\right) - c(A^2 - a^2) \frac{\pi}{2} \right],
 \end{aligned}$$

V_1 is obtained from V by replacing c by c_1 ,

$$c = l + l_1 \text{ and } c_1 = l - l_1,$$

$2l$ and $2l_1$ are the respective lengths of the two solenoids. $F(k, \pi/2)$ and $E(k, \pi/2)$ are the complete elliptic integrals of the first and second kind to modulus k where

$$k^2 = \frac{4Aa}{(A+a)^2 + c^2},$$

A and a are the radii of the solenoids $F(k', \theta)$ and $E(k', \theta)$ are the incomplete elliptic integrals of the first and second kind to modulus k' and argument θ .

$$\begin{aligned}
 k' &= 1 - k^2 \\
 \sin^2 \theta &= \frac{(A^2 - a^2)^2 + c^2(A - a)^2}{(A^2 - a^2)^2 + c^2(A + a)^2}.
 \end{aligned}$$

The value of the self inductance of solenoids can be easily obtained from the expression giving the value of the mutual inductance by making the radii equal and the lengths equal. Putting $A = a$ and $l = l_1$, the above expression will reduce to

$$L = 4\pi n n_1 \left\{ \frac{c^4 + 4A^2 c^2}{3\sqrt{4A^2 + c^2}} F\left(k, \frac{\pi}{2}\right) + \frac{4A^2 - c^2}{3} \sqrt{4A^2 + c^2} E\left(k, \frac{\pi}{2}\right) - \frac{8A^3}{3} \right\}$$

A NEW METHOD FOR THE ABSOLUTE MEASUREMENT OF INDUCTANCE.¹

By E. B. ROSA.

WIEN has given several methods for measuring inductances in terms of resistance and time, and Anderson's method is an excellent one for measuring inductances in terms of capacity and resistance. I have found a method of using a condenser in series with one arm of an alternating current Wheatstone bridge while the inductance to be meas-

¹ Abstract of a paper presented at the Washington meeting of the Physical Society, April 19-20, 1907.

ured is in series with the opposite arm, such that when a balance is secured and the frequency of the current is accurately measured both the capacity and the inductance can be obtained in terms of resistance and time by a single setting of the bridge. This use of a condenser in series with the opposite arms differs from Wien's use of the condenser in parallel with the same arm in which the inductance is placed.

If a_1 , a_2 , a_3 , a_4 are the impedances in the several arms of the bridge, and R_1 , R_2 , R_3 , R_4 the corresponding resistances, L the inductance and C the capacity, we have for balance

$$a_1 a_4 = a_2 a_3$$

If the resistances are free from inductance and capacity, so that L and C are the only inductance and capacity in the bridge,

$$f^2 L^2 = \frac{R_1}{R_4} (R_2 R_3 - R_1 R_4)$$

$$f^2 C^2 = \frac{R_1}{R_4} \left(\frac{1}{R_2 R_3 - R_1 R_4} \right)$$

If, in order to eliminate small differences in the resistance and in the inductance or capacity of the two ratio arms, the two resistances R_2 and R_4 are made equal, the equations reduce to

$$f^2 L^2 = R_1 (R_2 - R_1)$$

$$f^2 C^2 = \frac{R_1}{R_4} \left(\frac{1}{R_2 - R_1} \right)$$

In interchanging R_2 and R_4 it is of course necessary to leave the condenser unmoved. In order to do this quickly without altering the resistance of the leads a special form of bridge has been devised.

The resistances are submerged in oil and slide wires attached for close settings. The method is well adapted for very precise measurements, using of course tuned galvanometers to be free from the effects of harmonics. The complete paper will be published in the Bulletin of the Bureau of Standards.

THE PHYSICAL REVIEW.

FATIGUE AND RECOVERY OF THE PHOTO-ELECTRIC CURRENT.¹

BY W. F. HOLMAN.

THE experiments of H. A. Wilson² showing that the escape of negative electricity from incandescent platinum disappears when the metal is freed from absorbed hydrogen; and those of Skinner,³ that in the glow current through rarefied gases hydrogen atoms serve as carriers of negative electricity from metallic cathodes to the gas, suggest the possibility of the absorbed gas playing a part in the escape of negative electricity from a metal subjected to ultra-violet radiation. In fact, the experiments of Wulf⁴ indicate that the presence of absorbed hydrogen increases the photo-electric current from platinum, in that after the platinum has been allowed to stand in an atmosphere of hydrogen for some time there is a marked increase of the current over that obtained in air and again a decrease as the metal supposedly loses its charge of hydrogen.

This photo-electric current depends on two principal factors, first that arising from the escape of negative carriers from the metal, and secondly, that from the ionization of the gas by these carriers. Thus the experiments of Stoletow,⁵ Lenard,⁶ and Varley⁷ show that as

¹ Read in part before the joint meeting of the American Physical Society and Section B of the American Association for the Advancement of Science, Ithaca, June, 1906.

² Phil. Trans., 202, p. 243, 1903.

³ Phys. Rev., XXI., p. 1, 1905; Phil. Mag., Nov., 1906.

⁴ Ann. d. Physik, 9, p. 946, 1902.

⁵ Jour. de Phys., 9, p. 468, 1890.

⁶ Ann. d. Physik, 2, p. 359, 1900.

⁷ Phil. Trans., 202, 1903.

the gas pressure is reduced indefinitely the photo-electric current drops to a definite minimum value which thereafter remains practically constant for all values of the electric field. This is considered as that arising solely from the carriers escaping from the metal. On the other hand when the discharge takes place in an atmosphere of appreciable density the current may be produced largely by the second factor, the ionization of the gas by the motion of these escaping carriers. For instance, Kreussler¹ found that in air at atmospheric pressure the current increases very rapidly with the electric intensity, if the latter approaches that required to produce a spark discharge.

The present investigation was undertaken therefore with the intention of studying the current arising from the escaping carriers alone, as it is affected by changing the store of hydrogen in the surface of the metal. The results were such as to include a study of certain phases of the so-called *fatigue* and *recovery* of the metal under the conditions of operation.

The plan which suggested itself as most likely to yield conclusive results was based on the discovery of Skinner that as cathode in a glow current, the metal gives off hydrogen, while as anode it absorbs it. In case therefore these conditions can be brought about without otherwise affecting the surface of the metal, this plan furnishes a simple scheme for making a test of the effect of changing the quantity of hydrogen in the metal. As will be seen, however, this condition was attained without question only in one series of experiments.

EXPERIMENTAL ARRANGEMENT.

Fig. 1 presents a diagram of the system used. An electric arc *A* operated, in parallel with a capacity *K*, by an induction coil fed by a fifty-volt alternating current served as source of light. This arc was focused by a quartz lens *L* through a window *Q* of same material on the cathode *E* charged from a battery *B*. The current of negative electricity from *E* to the anode *H*, placed opposite, was determined by measuring the rate with which a definite capacity *C*, connected to the latter, was charged. For this purpose a Thomson quadrant electrometer was employed in the customary manner.

¹ Ann. d. Physik, 6, p. 398, 1901.

The positive pole of the battery and the other terminal of the condenser *C* were connected to earth. Both the electrometer and the arc system were enclosed in grounded metal cases. Spurious effects were corrected for in all cases by taking observations with the electrode simply screened from the light, other conditions remaining the same.

The electrode chamber is shown in vertical section and plan in Fig. 2. It was designed for testing several metals successively. These were in form of disks *E* mounted on the face of a circular glass plate which could be rotated at will about a supporting axis of brass by means of the ground joint *D* and key *K*. The electrical connections were made through *J*, the supporting axis, and

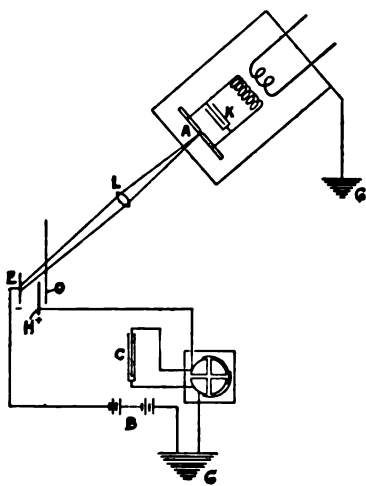


Fig. 1.

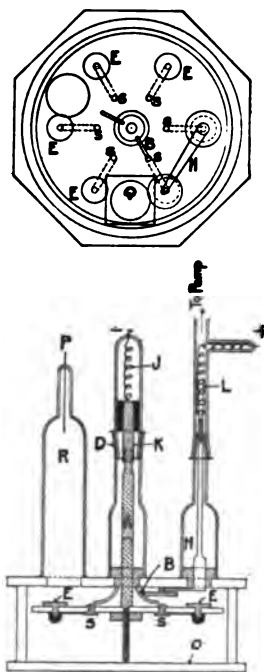


Fig. 2.

the spring brush *B* to the contact *S* connected, by tin foil strips placed under the plate, to the cathode *E*. The connection with the fixed aluminum anode was made through its supporting arm *H* and the wire *L*. In order to use the metals *E* as electrodes with a glow

discharge, a tube *R* with an additional electrode *P* was attached to the chamber as indicated. For this purpose a second spring brush similar to *B* served as connection. The arrangement was such as to insulate all electrodes except the one in action. All fixed joints which could not be fused were sealed with de Khotinsky's laboratory cement. The chamber proved to be perfectly air-tight. The electrodes could be renewed by removing the base plate *O*, which permitted the plate carrying them to be taken out.

In the vacuum system all stop-cocks and ground joints were lubricated with a mixture, recommended by Travers, free of hydrocarbons. Evacuation was produced by a Rapps automatic pump. A McLeod gauge multiplying the pressure about ten thousand times served as pressure indicator. P_2O_5 was used as dryer. A battery of small accumulators served as source of potential.

For an electric arc that found by Varley to be most satisfactory, namely steel electrodes in a slow stream of hydrogen, was used. It proved to be much more constant than other sources tried.

The capacity *C* (Fig. 1) consisted of an air condenser of tin foil mounted on plane glass plates insulated with quartz.

EXPERIMENTS.

Zinc, carefully polished and cleaned, was tested first. This was mounted in the electrode chamber which was immediately evacuated and left at an indefinitely low pressure in connection with the drying chamber for several hours.

With a gas pressure of .001 mm., a P.D. of about 500 volts¹ and a capacity *C* (Fig. 1) of about 1,400 cm., the photo-electric current produced in ten seconds the following series of deflections of the electrometer (8.5 scale divisions = one volt). The arc was stopped after each reading and started anew for the next.

TABLE I.

33.4	32.5	32.6
34.4	32.7	31.5
32.9	33.4	30.0
27.0	33.5	30.5
		Mean, 32.0

¹ At the pressures used the photo-electric current proved in all cases wholly independent of the magnitude of the P.D. between the electrodes.

This value is equivalent to 6×10^{-10} amperes. After admitting hydrogen at a pressure of 1.5 mm. a glow current was then sent from the zinc as cathode for about fifteen minutes, and the chamber again evacuated to a pressure less than .001 mm. The photo-electric current observed at this point gave the following successive values :

TABLE II.

20.2	20.2	20.4
20.5	16.1	19.8
20.2	19.5	20.6
20.2	20.6	21.1
Mean,		20.0

representing a current of 3.8×10^{-10} amperes, which is a marked decrease compared with the fresh metal.

After standing then twelve hours, the following series of observations were taken under the same conditions as before :

TABLE III.

21.3	20.9	21.7
21.5	21.8	22.7
21.3	21.9	22.5
17.7	22.7	22.3
Mean,		21.5

representing 4.1×10^{-10} amperes. This shows only a comparatively slight increase over the values obtained twelve hours before. Following this, hydrogen was again admitted and the metal used in this case as *anode* during a period of about seven minutes, after which the chamber was evacuated to less than .001 mm. and the following series of values obtained for the photo-electric current.

TABLE IV.

27.5	31.4	32.0
28.0	33.0	32.5
30.1	32.7	32.2
31.5	32.2	
Mean,		31.2

or a current of about 5.9×10^{-10} amperes which is strikingly close to the first values as given in Table I.

The above results are readily explained in the light of Skinner's experiments if we assume that hydrogen may also serve as carrier of negative electricity in the photo-electric current. With the unused

metal the photo-electric current was 6×10^{-10} amperes. By use as cathode with a glow current the quantity of hydrogen present was undoubtedly considerably reduced. The photo-electric current in this condition was also reduced to about two thirds its original value, 3.8×10^{-10} amperes. Left at rest for several hours the metal indicated practically no change from this last value, but after use as anode in hydrogen — which charges the metal with this gas — the photo-electric current returned to its original magnitude. The same explanation, however, may be given by assuming a migration of electrons with the negative current, if we assume the possibility of appreciably changing their available number in the metal in the same way as the quantity of hydrogen is changed.

A repetition of the above experiments with several different metals brought to light an entirely different set of influences. With electrodes freshly polished the electrode chamber was left at extreme vacuum in connection with the dryer for several hours, after which the photo-electric current was tested as before in an atmosphere of less than .001 mm. pressure. The mean results of a number of tests, in which the individual observations revealed about the same fluctuation in value as those in the previous experiments, are given in Table V. In this series the capacity C was about 2,800 cm., other conditions as before.

TABLE V.

	Photo-electric Current (10^{-10} Amperes).				
	Zinc.	Copper.	Silver.	Aluminium.	Iron.
After using as cathode with glow current in hydrogen.	16	11.6	6.4	0.6	0.6
After standing 12 hours in hydrogen.	8.8	1.8	14	0	0
After again using as cathode.	41	16		5	4.5
After using as anode in hydrogen.	7	15	6	1.3	1.4
After using as cathode again.	36	16.5	25	2.7	5
After standing in hydrogen several hours.	28	9.3	16	2.5	3.2

A striking feature in these results is the exceptionally large value of the photo-electric current of zinc as compared with the previous tests — the magnitude in one case being as much as seven times as great as the largest values before, and in no case dropping as low as the maximum value previously obtained. In these experiments

it is to be noted that after use as cathode the current is greatest, and after standing in hydrogen or used as anode, it is generally considerably smaller—the different metals being affected in different degrees. The probable explanation is that use as anode or even contact with the gas (possibly not entirely pure) tarnished the surface of the metal and this reduced, as is known, the photo-electric action. In action as cathode with the glow discharge the metal surface in these tests was probably cleaned of tarnish but not sufficiently depleted of its negative carriers to reduce the photo-electric current.

It was thought possible to obtain less complicated results by operating with the glow discharge in argon instead of hydrogen, since according to Skinner use as cathode in this gas serves to deplete the store of hydrogen while use as anode has no appreciable effect. The results obtained are recorded in Table VI. For these experiments, the capacity C was again reduced to 1,400 cm.

TABLE VI.

	Photo-electric Current (10^{-10} Amperes).				
	Zinc.	Copper.	Silver.	Aluminium.	Iron.
After standing <i>in vacuo</i> .	1.2	0.5	0.9	1.2	0.2
After use as anode with glow current in argon.	1.2	13	5	0.4	0.7
After use as cathode in argon.	19	11.6	6.3	1.4	0.7
After standing in hydrogen for several hours.	2.4	9	1	0.5	1.2

The effects here are very similar to those recorded in Table V. with the exception that the use of copper and silver as anode with a glow current in argon appears to clean the metal of its tarnish in that it increases its photo-electric current. It should be remarked that in no case did a *visible* tarnish appear when argon was used.

Although the results given in Tables I., II., III., and IV. could not be duplicated, they are so definite that it seems probable that the desired state of depletion of the metal by use as cathode was not reached in the later experiments. Unfortunately further prosecution of the investigation was impossible.

I wish here to express my thanks to Dr. C. A. Skinner of the University of Nebraska for his help and inspiration to me in this work. I am also grateful to Dr. J. E. Almy for much aid and many helpful suggestions.

COEFFICIENT OF LINEAR EXPANSION AT LOW TEMPERATURES.

BY HERBERT G. DORSEY.

IN the present investigation of the coefficient of expansion of substances a direct method of measuring the change in length is used and it is thought that to this end all corrections have been eliminated.

The fundamental idea in the method was first published by Fizeau in 1864 and later developed by Pulfrich in 1893, Tutton, 1898, and Ayers, 1905.

Fizeau¹ first used a tripod (Fig. 1) of steel screws which supported two plates, *D* and *E*. The upper one, *D*, carried a plate of glass, and the lower one served as a table to support the specimen, *F*, to be examined. The upper surface of *F* being polished, monochromatic light passing through *D* and meeting light reflected from *F* produced interference fringes. Any change in the length *FD* would cause a shift of the fringes. The method was devised primarily to examine the expansion of

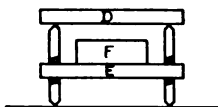


Fig. 1.

small and rare substances such as diamond. A correction had to be applied for the change in the length of the tripod screws and later he used an alloy of platinum-iridium as being more suitable.

Pulfrich² used practically the same method but worked out an elaborate correction for the change in wave-length of the light used due to variation in the density of the gas in the space *FD* due to change in temperature.

Tutton³ modified the method by placing between *E* and *F* a plate of aluminium of such thickness that it would compensate for the change in length of the tripod screws.

¹Compt. Rendus, Vol. 58, 1864.

²Zeit. für Inst., 1893.

³Phil. Trans., 191, A, 1898.

Ayers¹ made a great stride towards eliminating corrections by using a hollow cylinder of the material to be examined. By placing it upon a plate of glass and resting another plate above it, interference takes place between light reflected from the top of the bottom plate and the bottom of the top plate the only correction necessary is that due to the change in wave-length. This same method has been mentioned by Scheele² and acknowledged by Professor J. S. Shearer.¹ Ayers examined silver and aluminium down to liquid air temperatures, applying the correction by Pulfrich's formula.

Simpson¹ repeated Ayers' work with the same apparatus and exhausted most of the air so as to eliminate at least a part of the last correction. Beginning at this point the problem as presented to the writer was to eliminate entirely this last correction.

THE BOX.

After several unsuccessful attempts with gaskets of soft rubber and lead, and insulating plugs of rubber and ivory, a cylindrical box was turned from a piece of steel shafting and into the top was ground a piece of thick plate glass as a stopper in a bottle. This was ground in at a small angle so that reflected light would pass out of the field of vision. The joint being slightly lubricated with a mixture of tallow and beeswax will hold a vacuum down to liquid air temperature and when sealed in with shellac will hold up to steam temperature.

Near the bottom a seamless copper tube about 15 cm. long was soldered with silver solder and to the end of this was soldered a longer lead tube. The wires of the resistance thermometer were passed out in the tube and far enough away from the box to be at room temperature were passed through the lead tube, the joint being closed with shellac.

At the bottom of the box was left a tapering lug of steel to conduct the heat from the box slowly. Later a ring of wires of varying lengths was attached. With this arrangement, since the box weighs only about 175 grams, it can be held at any temperature for any desired length of time, and only about a liter of liquid air is necessary for a test of six or eight hours.

¹ PHYS. REV., Vol. XX., Jan., 1905.

² Ann. d. Phys. (4), 9, 1902.

THERMOMETER.

Temperatures are measured with a copper resistance thermometer. On a spool of fine silver 2 cm. internal diameter and 0.7 cm. long were wound several layers of No. 36 single silk covered copper wire. To the ends were soldered about 50 cm. of No. 22 double cotton covered wire and to these ends flexible lamp cord of No. 16 equivalent size. To the ends of the flexible cord copper pieces were soldered for terminals. The junctions of the cord and No. 22 are kept wrapped in wool and no thermal effects have been noticed.

The resistance of the thermometer was measured by a Wheatstone bridge, a portable testing set, decade pattern being used in connection with a sensitive reflecting D'Arsonval galvanometer and a Leclanche battery. The same ratio coils, 10 to 1,000, were used both in calibrating the thermometer and in the experimental work. As a further check every coil of the testing set was measured on a bridge correct to 0.1 per cent. and the percentage errors of the testing set computed. The greatest possible error of any combination of coils in the testing set is 0.87 per cent.

In the preliminary calibration dummy leads were run to the coil. Resistance of coil and leads was 67.56 ohms at ice temperature and leads alone 0.182 ohm; coil in liquid air 11.98 ohms, leads alone 0.166 ohm. Thus the change in resistance of the coil alone was 55.56 ohms and for the leads 0.016 ohm in a change in temperature of 190°. The error, then, which would be introduced by neglecting the change in resistance of the leads would not be over 16 parts in 55,000, or about 0.03 per cent. And since the same lead wires have been used throughout the experiment they are considered a part of the thermometer.

The ice temperature resistance of the thermometer on April 15, 1905, was 67.56 ohms. This was after remaining in distilled water ice thirty minutes, the battery key being left closed all the time. It was noticed later in liquid air tests that with the battery key left closed there was a slight but distinct warming of the coil so that in subsequent measurements the battery key was closed only long enough to produce the galvanometer deflection if any.

On March 14, 1906, resistance in ice with battery key closed only momentarily was 67.53 ohms. Two days later, in fresh, clean snow

resistance was 67.53 ohms. The ice point resistance was taken as 67.53 ohms, and as the two measurements made about a year apart are so nearly alike, a stable condition of the thermometer is indicated.

The low-temperature points were taken from a curve plotted between the resistance of the coil and temperatures of liquid air as

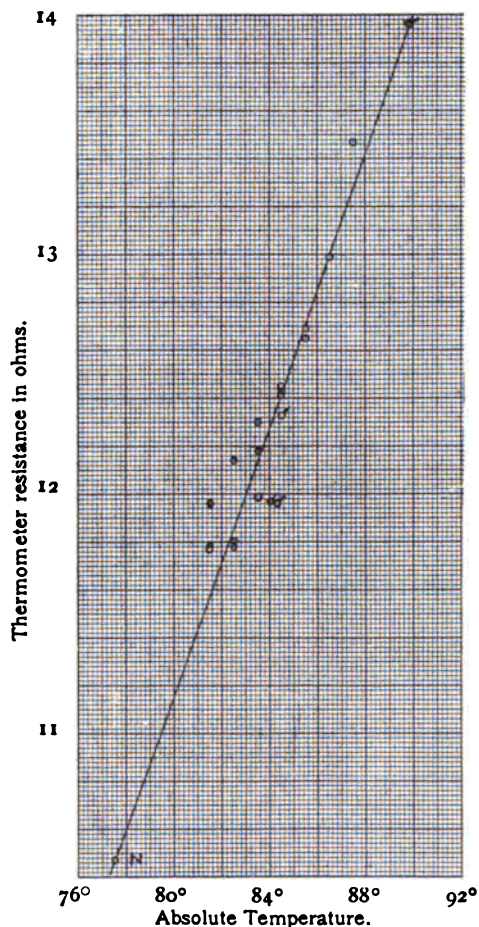


Fig. 2.

indicated by air analysis and Baly's¹ curve and "schwimmers"² and liquid nitrogen.

¹ Phil. Mag., Vol. 49, 1900.

² Ann. d. Phys., p. 421, 1903.

In Table I. is given the data from which Fig. 2 is plotted. In the curve the air analysis points are marked with a circle and dash.

TABLE I.

Date.	Corrected Resistance.	Temperature.	Method.
April 15, 1905.	11.96	84.3°	Air analysis.
"	11.97	84.0	"
May 26, 1905.	12.33	84.5	"
February 28, 1906.	11.99	83.5	Schwimmer floating.
March 16, 1906.	11.77	81.5	" beginning to float.
"	11.78	81.5	" floating.
"	11.80	82.5	" beginning to float.
"	11.78	82.5	" floating.
"	12.30	83.5	" "
"	12.45	84.5	" beginning to float.
"	12.69	85.5	" " "
"	12.99	86.5	" " "
"	13.47	87.5	" " "
March 19, 1906.	13.96	89.8	Air analysis.
April 6, 1906.	11.96	81.5	Schwimmer floating.
"	12.14	82.5	" "
"	12.18	83.5	" beginning to float.
"	12.43	84.5	" floating.
"	12.65	85.5	" "
"	12.41	84.5	" "
April 14, 1906.	10.47	77.5	Liquid nitrogen.

To determine the steam point the coil was immersed with a Baudin thermometer in a long tube of kerosene and this placed in a jacketed steam bath. Temperatures were taken from the thermometer, the latter being corrected for stem exposed, and for true boiling point determined by barometer. Barometer was corrected for temperature, meniscus and scale reading and difference between values of gravity at Paris and Ithaca. A single careful determination made on March 16, 1906, gave resistance = 96.00 ohms for temperature of 372.12°. On April 11, 1906, under similar conditions six determinations were made, a curve plotted and from this curve the resistance = 95.75 ohms for temperature of 371.00°. On this same date seven determinations were made at room temperature and from a curve plotted the resistance = 73.35 ohms for temperature of 293.00°. These curves are not given as they are of less general interest than the low temperature points.

From the values

Temp. abs.	Res.
372.12°	96.00
371.00°	95.75
293.00°	73.35
273.00°	67.61
83.00°	11.99
77.50°	10.47

an equation was determined, $R = 67.61 + .28904t - .00001913t^2$ (where t is expressed on Centigrade scale). From the equation the resistance was calculated for every 20° from 373° to 93° and a large curve plotted so that temperatures could be read to 0.1°.

MEASUREMENTS OF LENGTHS.

From the theory of interference in thick plates it is necessary that the surfaces be nearly parallel if the interference bands are to be wide. To realize this condition the specimen, in the form of a hollow cylinder, is cut away slightly at each end leaving three small projections. These are then adjusted by fine grinding and measuring until planes passed through them at both ends will form an angle of about 10 or 20 seconds of arc.

The measurements were made with micrometer calipers which were compared at 22° C. on a Rogers and Ballou dividing engine with a W. A. Rogers bar meter and yard. After applying bar and temperature corrections according to Rogers' specifications the micrometer screw was found to give average readings 0.13 per cent. too small. Adding this amount to the specimen measurements gives their lengths in terms of the Metre des Archives.

1.	2.	3.
1.1258	1.1243	1.1258
1.1254	1.1245	1.1252
1.1255	1.1242	1.1256
1.1259	1.1240	1.1255
1.1254	1.1240	1.1259
1.1256	1.1242	1.1254
Average = 1.1251		
Subtract .0005 (zero error)		
1.1246		
add 0.13 per cent. .0015		
length = 1.1261 cm.		
Temperature = 22° C. = 295 abs.		

At least five measurements of each of the three projections were made for each specimen and the average of the three sets taken. A sample of the measurements is given on previous page which is for gold as first tested.

ARRANGEMENT OF APPARATUS.

The general arrangement of the apparatus is shown in Fig. 3. Light from a mercury vapor lamp at *A* passes through a slit and is made parallel by the lens *B*. Passing through the prism *C* set

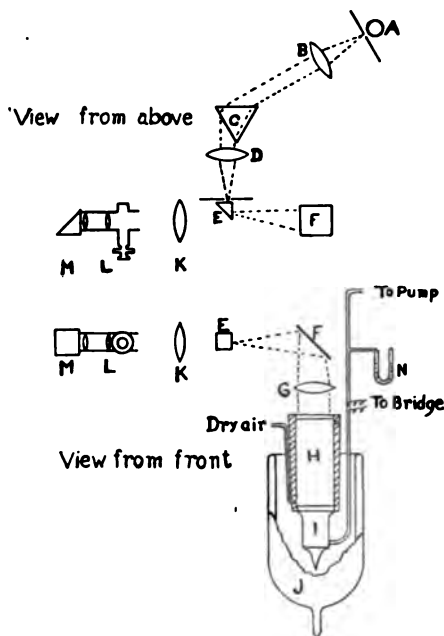
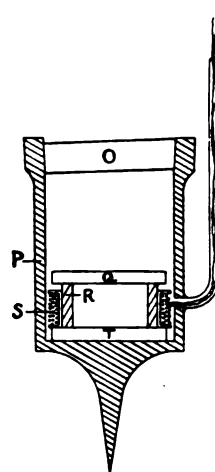


Fig. 3.



Section of box

Fig. 3a.

for minimum deviation, the lens *D* focusses it on a very small slit and by the right angle prism *E* it is reflected to the mirror *F* silvered on its front surface. Thus far the light paths are horizontal, but the mirror *F* reflects it downwards and the lens *G* again renders it parallel. After passing into the box *I*, producing interference bands it is brought to a focus at *E*, just at the edge of the prism. The lens *K* produces a real image of the fringes at the plane of the cross wires in the micrometer eye-piece *L* and another right angle prism *M* reflects the light to the eye.

In the section of the box the interference fringes are formed at the lower surface of the glass wedge *Q*. On this surface two fine crossed lines were scratched which serve as a reference point. *T* is a disc of black glass polished on its upper surface only upon which rests the specimen *R*. *S* is the resistance thermometer and *O* is the glass window of the box.

The box is held by friction in the wooden tube *H*. To keep the window *O* from frosting over dry air is passed in at the bottom of the tube *H* and out at the top, the upper end being closed by a glass plate. The best and most convenient source of dry air yet found is obtained from the slowly evaporating liquid air in a Dewar bulb.

The cylindrical Dewar bulb *J* containing liquid air for cooling is raised or lowered by a hand wheel on the axle of which is wound a strap carrying a balanced platform which carries the bulb.

The box is exhausted by a mercury pump and a manometer *N* is placed so as to be easily seen. The Wheatstone bridge is placed on the table in front of the observer so that adjustments can be easily made with the left hand, leaving the right to control temperature. The scale of the galvanometer is in line with *M*, so that the spot of light can be observed without turning the head.

METHOD OF OBSERVATION.

The specimen being sealed in the box and adjusted to give good interference fringes, the box is exhausted to something less than a mm. pressure and the Wheatstone bridge set for some given temperature. The box is then warmed or cooled until the spot of light remains stationary at zero and the fringe system ceases to move. Usually no dark band will be on the reference mark so its distance is measured as a fraction of the distance between two dark bands. The box is then rapidly cooled (or warmed) and the bridge set for the next temperature. Meanwhile the fringes are counted as they pass the reference mark by pushing the handle of a counting machine. The box will soon have reached the desired temperature and is held there until the fringe system stops moving. This occurs nearly the same time that the galvanometer comes to zero. For the amount of matter in the specimen is so small, only a few

grams, and it is so near the thermometer, being surrounded by it, that it very quickly comes to the same temperature. The entire time occupied in covering a 20° interval is usually 20 to 30 minutes. After all motion has ceased the fringe fraction to be added

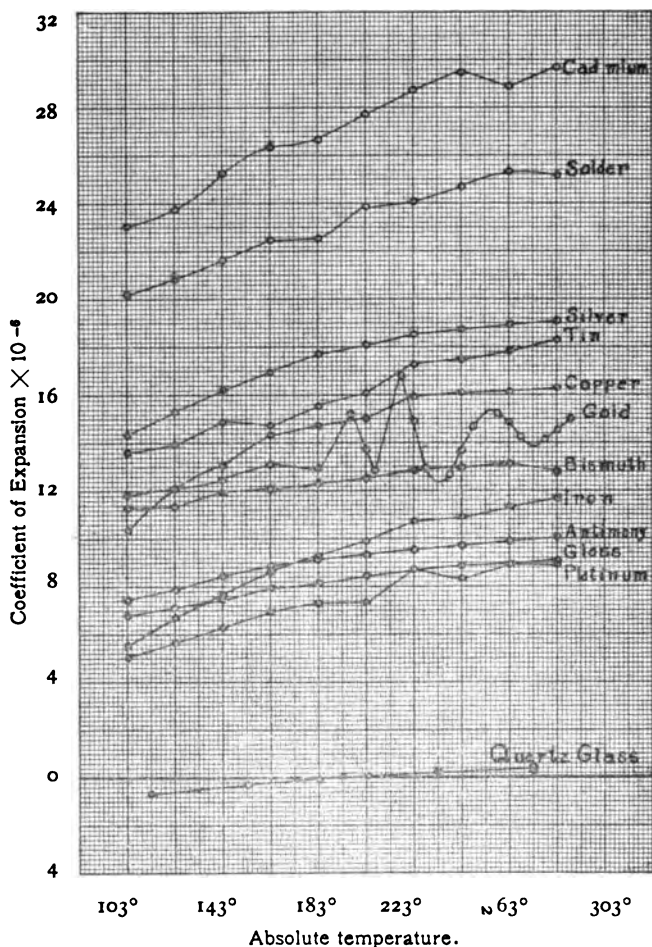


Fig. 4.

is measured and that with the number on the counter and the resistance is recorded.

This process is repeated by 20° intervals down to 93° and then again as the box is warmed to room temperature. Thus the change in length is measured both in cooling and warming the specimen

and the average of all the measurements for any given interval gives the amount used in calculating the coefficient of expansion for that interval.

Since the light passes the length of the specimen twice a whole fringe counted means an actual change in length of one half the wave-length of light used so that the coefficient is $e = n\lambda/2dt$ where n is the number of dark spaces counted, λ the wave-length, d the length of the specimen, and t the temperature interval, usually 20° . The green line of mercury was used, the wave-length of which is $54,607 \times 10^9$ cm., according to Fabry and Perot. The coefficient thus determined is taken as the average for the temperature interval and is plotted at the middle of the interval in Fig. 4.

Table II. gives the middle temperature of the interval, that at which the coefficient is plotted, the number of fringes counted and their average, the calculated coefficients, average coefficient between 293° and 93° , and description of material.

TABLE II.
Antimony. Cast.

From Department of Chemistry, marked chemically pure. Length = 1.3409 cm. Average width fringes = 180 divisions of micrometer eye-piece head. Density = 6.88. Average coefficient from 293° to $93^\circ = 8,170 \times 10^{-8}$.

As shown in the table, the specimen actually expanded more on warming than it contracted in cooling.

Temp.	283°	263°	243°	223°	203°	183°	163°	143°	123°	103°
Cooling.	10.04	8.59	8.75	8.66	8.56	8.17	7.82	7.05	6.41	6.16
Warming.	9.78	10.66	9.84	9.77	9.31	9.28	9.22	8.61	8.22	8.00
Cooling.	10.13	10.06	9.97	9.92	9.65	9.19	8.89	8.57	8.18	7.37
Warming.						9.25	8.91	8.84	8.31	7.89
Cooling.	9.86	9.57	9.63	9.30	9.16					
Average.	9.95	9.72	9.55	9.41	9.17	8.97	8.71	8.27	7.78	7.35
$e \times 10^{-8}$.	1,009	988	970	956	933	913	886	841	791	747

Cadmium. Cast.

From Eimer and Amend, marked pure. Length = 1.1659 cm. Average width fringes = 200. Density = 8.62. Average coefficient = $2,692 \times 10^{-8}$. Coefficient corrected for change in length at lower temperatures

	25.39	24.28	25.16	24.78	23.33	22.63	22.48	21.48	20.38	19.67
	25.56	24.73	25.17	24.78	23.78	22.61	22.38	21.50	20.23	19.33
	25.32	24.94	25.20	24.19	23.65	22.77	22.52	21.57	20.00	19.64
	25.16	24.77	25.18	24.37	23.51	22.71				
						22.73				
Average.	25.38	24.68	25.18	24.53	23.57	22.69	22.46	21.52	20.20	19.55
$e \times 10^{-8}$.	2,970	2,890	2,948	2,876	2,768	2,664	2,638	2,527	2,379	2,302

Bismuth. Cast.

From Department of Chemistry, marked Free from Arsenic. Length = 1.3409 cm. Average width fringes = 170. Density = 9.84. Average coefficient = $1,224 \times 10^{-8}$.

Temp.	285°	265°	245°	225°	205°	185°	165°	145°	125°	105°
	14.50	14.73	14.58	14.49	14.07	13.78	13.49	13.37	12.65	12.69
	14.60	14.76	14.49	14.40	14.14	13.88	13.53	13.56	12.93	12.71
	14.26	14.79	14.73	14.55	14.03					
	14.24									
Average.	14.40	14.76	14.60	14.48	14.08	13.83	13.51	13.46	12.79	12.70
$\epsilon \times 10^{-8}$.	1,280	1,311	1,298	1,287	1,251	1,230	1,201	1,196	1,136	1,129

Copper. Commercial seamless tubing.

Analyzed by Mr. C. G. Schluederberg, fellow in chemistry, and found to be 99.9 per cent. copper. Length = 0.9712 cm. Average width fringes = 190. Density = 8.91. Average coefficient = $1,102 \times 10^{-8}$.

	11.80	11.34	11.50	11.00	10.59	10.44	10.31	9.49	8.59	7.69
	12.05	11.47	11.34	11.61	10.80	10.69	10.24	9.44	8.40	7.35
	11.50	11.40	11.94	11.16	10.65	10.51	10.00	9.16	8.72	7.26
	11.40	11.14	11.55	11.51		10.25	10.19	9.25	8.57	7.24
	11.63	11.69	11.09	11.55		10.31	10.00	9.25	8.70	7.43
	11.72	11.79	11.81	11.28			9.98	9.18	8.55	7.37
	11.30		10.90				10.77			
Average.	11.63	11.47	11.45	11.35	10.68	10.44	10.21	9.29	8.59	7.39
$\epsilon \times 10^{-8}$.	1,635	1,613	1,610	1,595	1,500	1,468	1,437	1,305	1,206	1,039

Glass. Crown tubing.

Length = 0.9673 cm. Average width* fringes = 230. Density = 2.45. Average coefficient = 736×10^{-8} .

	6.37	6.40	5.74	6.26	5.00	5.06	4.88	4.57	3.97	3.69
	6.40	6.50	5.98	6.34	5.40	5.20	5.02	4.22	3.88	3.40
	6.50	6.16	6.00	5.94		5.24	5.00	4.44	4.04	3.63
							4.73	4.61	4.07	3.63
Average.	6.42	6.35	5.91	6.18	5.20	5.17	4.91	4.46	3.99	3.59
$\epsilon \times 10^{-8}$.	906	892	835	873	734	730	694	630	563	507

Gold. Cast.

Analysis by Mr. Schluederberg gave 99.0 per cent. gold and traces of platinum. Length = 1.1261 cm. Average width fringes = 110. Density = 19.49. Average coefficient = $1,338 \times 10^{-8}$.

	12.06	12.25	11.15	12.68	11.33	10.21	10.89	10.92	10.19	9.63
	11.83	12.25	11.41	12.18	11.75	10.70	10.10	9.40	9.60	9.73
				12.00	11.09	10.26	10.93	10.83	9.59	9.91
					11.23	11.04	10.96	10.45	10.27	9.73
					11.18	11.19	10.77	9.64		
Average.	11.95	12.25	11.28	12.29	11.31	10.68	10.73	10.25	9.91	9.75
$\epsilon \times 10^{-8}$.	1,450	1,486	1,368	1,488	1,373	1,294	1,301	1,242	1,201	1,182

Gold, same as above, but different temperatures. Length = 1.1253 cm. Average width = 100.

The surprising irregularities given by the first test were checked by a second test which gave intermediate points on the curve, thus verifying the first test.

Temp. Interval	294.5° to 284.8°	284.8° to 273°	273° to 263°	263° to 253°	253° to 243°	243° to 233°	233° to 223°	223° to 213°	213° to 201.3°	201.3° to 193°
Plot at	289°	278°	268°	258°	248°	238°	228°	218°	207°	197°
	6.08 5.90	6.95 6.84	5.80 5.82	6.25 6.16	5.93 5.78 6.28	5.31 5.14 5.01	5.11 5.48	6.98 6.72	5.95 6.43	5.41 4.99
Average.	5.99	6.89	5.81	6.21	5.99	5.15	5.29	6.85	6.19	5.20
$e \times 10^{-8}$.	1,500	1,416	1,425	1,524	1,470	1,263	1,298	1,680	1,282	1,520

Iron. Rolled rod.

From Pennsylvania Steel Co. Analyzed by Mr. Blough, formerly of the department of chemistry, and found to contain carbon, 0.058 per cent.; phosphorus, trace; silicon, 0.008 per cent.; manganese, 0.071 per cent. Length = 2.0129 cm. Average width fringes = 200. Density = 7.77. Average coefficient = 925×10^{-8} .

Temp.	283°	263°	243°	223°	203°	183°	163°	143°	123°	103°
	17.34 17.25 17.27	16.75 16.73 16.74	16.07 16.08 16.07	15.84 15.84	14.63 14.61	13.58 13.66 13.72	12.40 12.81 12.85	11.29 11.13 11.43	9.84 9.90 10.00	8.16 8.42 8.02 8.17
Average.	17.29	16.74	16.07	15.84	14.62	13.65	12.69	11.28	9.91	8.19
$e \times 10^{-8}$.	1,172	1,136	1,090	1,074	992	925	860	765	673	556

Platinum. Hammered. Commercially pure.

Specimen loaned by Messrs. J. Bishop & Co., Malvern, Pa. Length = 1.5112 cm. Average width fringes = 500. Density = 22.15. Average coefficient = 815×10^{-8} .

	9.84 9.93 9.88 9.83	9.87 9.80 9.81 9.91	9.82 9.89 9.72 9.89	9.72 9.69 9.63 9.58	9.35 9.29 9.33 9.29	9.07 9.12 9.06 8.94	8.81 8.88 8.84 8.82	8.36 8.27 8.26 8.26	7.88 8.02 7.98 7.97	7.57 7.58 7.54 7.49
Average.	9.87	9.85	9.83	9.65	9.31	9.05	8.84	8.29	7.96	7.54
$e \times 10^{-8}$.	891	889	887	871	841	817	798	748	719	680

Silver. Cast.

Pure, from United States Mint. Length = 1.2805 cm. Average width fringes = 190. Density = 10.43. Average coefficient = $1,740 \times 10^{-8}$.

Temp.	283°	263°	243°	223°	203°	183°	163°	143°	123°	103°
	17.92	17.76	17.58	17.45	16.95	16.47	15.84	15.29	14.37	13.45
	17.94	17.85	17.61	17.49	17.27	16.86	16.00	15.13	14.40	13.53
	17.93	17.78	17.67	17.35	16.77					
Average.	17.93	17.79	17.62	17.43	16.99	16.66	15.92	15.21	14.39	13.49
$e \times 10^{-8}$.	1,910	1,891	1,875	1,855	1,809	1,773	1,696	1,620	1,530	1,435

Soft Solder. Cast.

Commercial "half and half" (tin and lead). Length = 1.8080 cm. Average width fringes = 130. Density = 8.72. Average coefficient = 2301×10^{-8} .

	33.10	33.75	32.75	31.75	31.87	29.75	29.43	28.43	27.71	26.50
	33.80	33.30	32.70	31.85	31.25	30.00	29.80	29.00	27.64	26.60
						29.52		28.10		26.96
								29.00		26.43
								28.55		
								28.12		
Average.	33.45	33.52	32.72	31.80	31.56	29.76	29.61	28.53	27.68	26.62
$e \times 10^{-8}$.	2,515	2,530	2,470	2,409	2,388	2,255	2,245	2,162	2,080	2,020

Tin. Cast.

From Eimer and Amend, marked chemically pure. Length = 1.4332 cm. Average width fringes = 220. Density = 7.32. Average coefficient = $1,585 \times 10^{-8}$.

Since tin is meta-stable at ordinary temperatures and is subject to a slow change to a less dense "gray tin," it was watched carefully, but no great irregularity was observed.

	19.00	18.33	17.92	18.10	16.90	16.50	15.50	15.64	14.60	14.20
	19.29	19.18	18.76	18.23	16.64	16.21	15.00	15.68	14.69	14.37
	19.13	18.90	18.00	18.00	17.12	16.19	15.90	15.49	14.65	14.24
	19.00	18.32	18.27							
Average.	19.10	18.68	18.24	18.11	16.89	16.30	15.47	15.60	14.65	14.27
$e \times 10^{-8}$.	1,832	1,780	1,746	1,729	1,609	1,554	1,473	1,488	1,395	1,361

Quartz Glass.

Cut from tubing. Clear, but not transparent. Length = 1.4917 cm. Average width fringes = 250. Density = 2.01. Average coefficient = -4.25×10^{-8} .

Temperature.	273°	233°	203°	183°	153°	113°
	1.00	.66	.09	-.06	-.70	-1.49
	1.01	.70	.07	-.10	-.60	-1.44
	.99	.61	.06	-.06	-.65	-1.48
	1.01		.02		-.66	-1.48
	1.01					
Average.	1.005	.66	.06	-.07	-.65	-1.47
$e \times 10^{-8}$.	46.0	30.2	5.48	-6.40	-29.8	-67.2

Quartz Glass.

Cut from mercury vapor lamp. Clear and transparent as glass. Length = 1.4591 cm. Average width fringes = 300. Density = 2.20. Average coefficient = -8.71×10^{-8} .

Temperature.	273°	233°		193°	153°	113°
	.71	.48		-.10	-.63	-1.43
	.79	.48		-.11	-.50	-1.41
	.84	.45		-.09	-.47	-1.46
	.75	.40		-.11	-.92	-1.38
Average.	.77	.45		-.10	-.63	-1.42
$e \times 10^{-8}$.	36.0	21.1		-4.68	-29.5	-66.5

Both quartz specimens changed from a positive to a negative coefficient at about -80° C. Karl Scheel's equation¹ for quartz glass gives -46° for the changing point. Both specimens for about 60° on either side of -80° C. showed this peculiarity: above -80° when warmed they at first contracted slightly and then expanded, and when cooled they at first expanded slightly and then contracted. Just the converse of this was true for about 60° below -80° C. This could not be detected at room temperatures nor at liquid air temperatures, nor was it noticed in any other substance. It is as though the coefficient were slightly negative or positive, depending on whether it was warmed or cooled.

ACCURACY.

At any temperature worked the resistance of the thermometer can be measured to 0.01 ohm and for a 20° interval this is about ± 0.17 per cent.

¹ Verh. d. Phys. Ges., 9, 1907.

Fringes can be measured to 0.02 fringe and in some cases to 0.01 fringe so that in a 5 fringe interval it would be ± 0.4 per cent. For most specimens the intervals had more than five fringes.

Lengths of specimens can be measured to 2 parts in 10,000 or ± 0.02 per cent.

Combining these by square root of sum of squares gives an error of ± 0.44 per cent. and these errors individually are all compensating errors. About the only error which might be introduced which is not compensating is change in wave-length which would be due to leakage. Considerable work was done on the index of refraction of air, oxygen, nitrogen and carbon dioxide at different temperatures in May, 1906, with this apparatus, which with further work will be published later. It was found that if the pressure actually changed 0.1 cm. during a 20° interval at the lowest temperature the error introduced due to change in wave-length would be only about 0.1 per cent. But no such change of pressure is allowed for a stroke or two of the mercury pump is made before each reading so that the pressure remains the same within one or two hundredths of a cm.

The above sources of error are thought to be the only ones inherent to the method. Individual intervals for some specimens, however, show differences among themselves far in excess of the above indicated errors. Generally it was tried to compensate these discrepancies by several measurements. Some of them may be due to individual peculiarities of the substance. Zinc, for example, shows actual sudden jumps of fringes at some temperatures. Data for it will be given in a future paper.

Considering these discrepancies it is thought that all results are accurate within 2 per cent. and the average coefficients between 293° and 93° within 0.1 per cent.

The work will be continued for other substances and alloys.

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THE EFFECT OF TEMPERATURE UPON THE DISCHARGE OF ELECTRICITY FROM METALS ILLUMINATED BY ULTRA-VIOLET LIGHT.

BY GEORGE WINCHESTER.

I. INTRODUCTION.

THE influence of temperature upon the discharge of electricity from metals illuminated by ultra-violet light has been studied by Hoor,¹ Stroletow,² Elster and Geitel,³ Righi,⁴ Zeleny⁵ and J. J. Thomson.⁶ The early investigations did not produce results capable of definite interpretation because in those experiments a gas surrounded the metal and its influence and effects were unknown. Hoor and Stroletow obtained conflicting results—Hoor found that the current from a zinc surface decreased as the temperature rose and Stroletow found the current rising with the temperature. Elster and Geitel found that the current from zinc was independent of the temperature. Righi found that the positive charge taken up by a hot plate was greater than that taken up by a cold plate; air currents set up by the hot metal may have influenced this result. Zeleny's results from experiments upon iron and platinum at atmospheric pressure bring out several interesting phenomena yet they shed no light upon the question of whether or not there is any change in the photo-electric effect due to a change in the temperature of the molecule, because of the unknown influence which the surrounding gas might have on the results. Elster and Geitel found that the current from a potassium surface in a good vacuum when its temperature changed from 20.3 to 50.3 was increased

¹ Hoor, *Wien. Berichte*, Vol. 97, p. 719, 1888.

² Stroletow, *Comptes Rendus*, Vol. 108, p. 1241, 1889.

³ J. Elster and H. Geitel, *Wied. Ann.*, Vol. 48, p. 625, 1893.

⁴ Righi, *Atti. Ist. Ven.*, 7-Mem. 11.

⁵ Zeleny, *PHYS. REV.*, Vol. 12, p. 321, 1901.

⁶ J. J. Thomson, *Conduction of Electricity through Gases*, p. 239.

nearly 60 per cent. J. J. Thomson in his book on Conductivity of Electricity through Gases refers to some work by himself in which the alkali metals were heated to a temperature of about 200° C. in a good vacuum ; he also found a very great increase in the current. E. Ladenburg¹ investigated the relative rates of discharge from the ordinary metals in a high vacuum but did not alter the temperature. He found that the rate of discharge depended much upon the condition of the electrode ; *i. e.*, upon the method and degree of polish of the surface ; also, that the value changed with the time. Just what change is produced in the electrode so as to alter the photo-electric effect he does not make clear.

The principal object in the present investigation has been to find out whether or not there is any temperature effect when the disturbing influence of the surrounding gas has been removed ; *i. e.*, with an increase of energy of translation of the molecule is there also an increase of subatomic energy shown by an increased photo-electric effect ? In the preparation of the metal disks as well as throughout the experiment, care was taken that all the different metals received the same treatment, and that the ultra-violet light acted upon the different metals under exactly similar conditions.

II. DESCRIPTION OF APPARATUS.

The apparatus which is shown in Fig. 1 consisted of a large glass bulb (Fig. 2) within which was mounted a circular aluminium disk used as a support for the different metals employed. The wheel was under magnetic control so that any metal might be rotated to a position in front of the source producing the ultra-violet light. The wheel was mounted on agate bearings and was balanced so that it would remain at rest when rotated into any position. Across the back of the wheel was fastened a small bar magnet to facilitate its rotation, which was accomplished by means of a large horse-shoe magnet ; in order that the wheel might be connected to the electrode outside the bulb, a platinum spring was used to place it in contact with the frame as is shown in the figure. The frame was in direct connection with the electrode. Metal disks of copper, nickel, iron, zinc, silver, magnesium, lead, antimony, gold, aluminium and brass,

¹ E. Ladenburg, *Ann. d. Phys.*, Vol. 12, p. 558, 1903.

each disk one centimeter in diameter, were attached to the circumference of the wheel. The disks were screwed to the aluminium wheel and polished with dry emery so as to be free from the presence

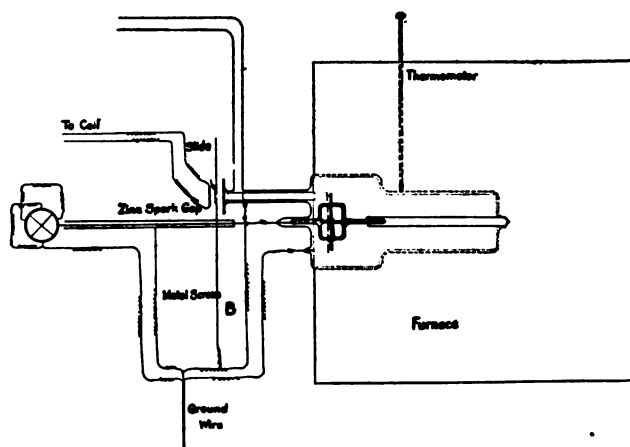


Fig. 1.

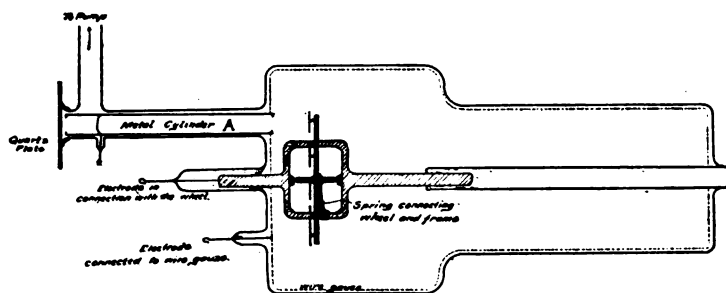


Fig. 2.

of any oils which might influence the photo-electric effect. They were finally heated, washed in alcohol, heated again, and mounted within the glass bulb without having their surfaces touched. Around the inner surface of the bulb and enclosing the wheel was placed a brass wire gauze which could be connected to earth or to the electrometer whichever was desired. In order that the different disks might occupy the same position with respect to the source of light and the wire gauze when they were exposed to the influence of the light, they were made to rotate in the same plane to within one one-thousandth of an inch or less. The ultra-violet light was admitted

to the bulb through a quartz plate sealed over the end of a projecting tube about 10 cm. long ; within this glass tube was placed a co-axial brass cylinder, *A*, whose inside surface was coated with a dull black finish to avoid reflection and to prevent any photo-electric effects from its surface ; its ends were closed with stops having openings of about 8 mm. diameter ; it could be connected to earth or to the electrometer just as in the case of the wire gauze ; the cylinder was placed close to the wheel so that the light would strike the disk which was being used and no part of the aluminium wheel would receive any light. Between the quartz plate and the source of light was a large metal screen, *B*, connected to earth, with an opening for the light ; the opening was furnished with a shutter with which it was closed before an observation was taken and while the tests for inductive effects, etc., were being made.

The pump used to exhaust the bulb was a type of mercury pump with all connections of glass and capable of producing a good vacuum. The measurements on the photo-electric effect were made at pressures of .00001 mm. or less, as recorded by a McLeod gauge ; the photo-electric effect was not influenced by pressures of this value as could be determined by working the pump until no gas could be pumped out and comparing values. Whenever a new bulb was sealed on, the temperature was always raised to about 400°C. at intervals ; and this was continued until no more gas was given off ; that this condition was realized was indicated by the fact that the gas from a bulb of 1,500 c.c. would collapse in a capillary tube of 1 mm. bore under a pressure of less than a centimeter of mercury ; at the same time the reading of the gauge would show pressures ranging from .00001 mm. to zero pressure. This is merely intended to show that the pressure was below that which would influence the photo-electric effect. The pump was always kept running throughout a series of observations to be sure that no gas collected in the bulb.

The electric furnace which was used to regulate the temperature was a box made of sheet-metal with heavy asbestos linings. Porcelain spools were covered with asbestos, wound with iron wire, and supported on the four sides and the bottom of the box. When the furnace was joined to a 220-v.circuit a temperature of 500°C. could

quickly be obtained. The amount of current was regulated by rheostats in series with the furnace.

A spark between zinc electrodes was used as a source of ultra-violet light. At first considerable difficulty was experienced in obtaining results which would check within ten or twenty per cent. under apparently the same conditions. It was thought that the variations in the deflections of the electrometer needle could be accounted for by the unsteadiness of the hammer of the induction coil. Several devices, including a mercury-turbine interrupter, were substituted for the hammer but without success. Finally it was noted that the irregularities could be accounted for in the leak of the electrometer itself. When this was corrected the readings could be duplicated to within one or two per cent. A variable capacity was used in connection with the coil so that the character of the spark might be somewhat altered when necessary.

As a source of constant potential a battery of 900 elements was used; this was made of copper-zinc strips in water with one or two drops of H_2SO_4 added to every liter of water. This source of potential would remain constant for months at a time — or so long as the battery was kept dry and well insulated. This battery was used to charge the needle of the electrometer and the metal disks.

One of the most serious difficulties encountered in carrying out this experiment was due to the humidity of the atmosphere during the summer months, when the work was done. This was so great that the use of any of the best insulators was of no avail in retaining the small charges generated. Sulphur would insulate extremely well, but its use had to be dispensed with because it could not be made to form a plug that would not leak air when a high vacuum was obtained. The small amounts of electricity generated would leak over a length of 20 cm. of small quartz rod, even when heated and a small stream of dry air kept blowing over the rod. As a last resort it was decided to enclose the entire apparatus in a room made of building paper and attempt to dry the enclosure. The room was built and trays of H_2SO_4 and CaCl_2 were distributed throughout. Also a stream of dry air was kept continually flowing into the room. Tubes were inserted in the walls for the observer to breathe through. That this method of stopping the leak was capable of giving quite satisfactory results will be seen farther on.

III. OBSERVATIONS OF THE RELATION BETWEEN THE RATE OF DISCHARGE AND THE TEMPERATURE OF THE METAL.

In making these observations the wheel was joined to one pair of quadrants of the electrometer, while the other pair was joined to earth. The quadrants and the wheel were connected to the negative pole of a battery of 20 cells (20 volts), the positive pole being earthed, and a certain deflection was produced; the connection was then broken, the induction coil started, and finally the shutter was raised and the light was left on for 10 seconds; the needle came to rest again in perhaps 60 or 90 seconds, and the difference between the two deflections was taken as the leak due to the photo-electric effect. The leak of the electrometer was so small as to be inappreciable in comparison with that due to the light, so long as the temperature remained below 100° C. At temperatures above 100° C. a correction had to be made to eliminate the natural leak, which at 170° C. had become so large as to mask entirely the effect of the light. The cause of this leak is unknown. Positive and negative charges would disappear with equal readiness.

When an observation was made a certain temperature was established by means of the furnace and held steady by altering the current; then the wheel was rotated and the different metals were exposed in turn to the influence of the ultra-violet before the quartz window. Sometimes two or more series of readings would be taken before the temperature was changed in order to see if the values could be duplicated. The observations could be checked over a time of two weeks as closely as they could at any one time. The following table shows a representative series of observations. Here the metals are arranged in the order of their ability to discharge negative electricity; about eight times out of ten the order was as given in the table; at other times the nickel and the brass changed places, as may be seen by looking at the table. Their values are so nearly alike that conditions could not be sufficiently controlled to discriminate between them. It would perhaps seem that if any of the metals were to change places in the table, due to their nearly equal values, it would be the brass and the copper, instead of the brass and the nickel. The order of the other metals was always the same. Also, the results were just the same, whether

the wheel was joined to the electrometer, and the gauze and metal cylinder earthed, or the wheel earthed and the gauze and cylinder joined to the electrometer.

TABLE I.

Metal.	Rate of Leak in Scale Divisions.							
	$T=25^{\circ}$	$T=35^{\circ}$	$T=40^{\circ}$	$T=50^{\circ}$	$T=65^{\circ}$	$T=80^{\circ}$	$T=100^{\circ}$	$T=125^{\circ}$
Cu	25.10	25.15	25.20	25.25	25.00	25.05	24.80	24.75
Au	24.70	24.60	24.55	24.70	24.80	24.75	24.40	24.00
Ni	24.00	23.96	23.98	23.90	24.05	23.90	23.55	23.40
Brass	23.80	23.85	23.95	24.00	23.85	23.90	23.40	23.40
Ag	17.16	17.20	17.15	17.20	17.10	17.00	16.90	16.77
Fe	16.40	16.25	16.30	16.20	16.36	16.55	16.15	16.00
Al	14.90	15.00	14.85	14.86	15.06	14.90	14.40	14.55
Mg	11.00	11.12	11.10	11.05	11.00	10.97	10.90	10.90
Sb	4.00	4.00	4.10	4.00	4.00	4.00	3.90	3.95
Zn	1.20	1.30	1.31	1.35	1.20	1.20	1.24	1.10
Pb	.90	.90	.90	.88	.90	.90	.90	.90

The table shows that up to 100° C. if there is an increase in the rate of discharge of electricity from these metals due to the increased temperature, it lies within the errors of the experiment. The readings at 100° C. and 125° C. were corrected for the temperature leak as explained below and are therefore weighted with a larger error than are the readings at the other temperatures.

In some experiments made in May, 1905, by Professor R. A. Millikan and the writer concerning the effect of ultra-violet light with change of temperature upon an aluminium surface, the temperature could be raised to at least 350° before any very decided effect due to the temperature was noticed, yet some other disturbing element was present which hindered very consistent results being obtained. At 400° the metal would not hold a charge at all. Below in Table II. is given a series taken Tuesday, May 30, 1905. It will be seen from the table that the results check over the entire range of temperature with about the same degree of accuracy that several readings do at any one temperature. It was concluded from observations like these that if there was any influence of the temperature on the photo-electric effect it must be rather small. The method employed in taking these observations was to observe the leak of the electrometer for 30 seconds, then

throw the light on for 15 seconds and take the deflection at the end of 45 seconds and finally to observe the leak during another 30-second period. The sum of the two electrometer leaks during the 30-second periods was then subtracted from the change in the electrometer readings during the intervening 60-second period and this remainder taken as the leak due to the light.

TABLE II.

Temp.	Deflection in Scale Divisions.	Temp.	Deflection in Scale Divisions.	Temp.	Deflection in Scale Divisions.	Temp.	Deflection in Scale Division.
49°C.	18.0	272°C.	14.3	304°C.	15.5	78°C.	20.3
50	16.3	275	14.2	310	15.8	75	19.3
50	17.4	280	14.0	343	15.4	73	20.6
100	16.0	286	13.8	343	17.0	69	20.9
142	14.2	290	15.1	256	16.9	67	20.8
169	17.0	292	15.4	200	18.0	64	21.6
191	16.5	295	15.2	170	17.1	61	20.4
205	16.6	296	16.2	143	17.3	58	20.5
215	16.3	297	15.7	130	18.1	54	20.9
220	17.2	298	15.9	120	17.4	54	20.1
233	12.9	300	15.7	112	19.2	53	20.4
246	14.2	301	16.3	105	17.5	52	20.8
254	13.6	300	15.8	100	17.6	52	19.6
260	14.0	301	16.6	95	19.2	53	17.3
264	13.9	301	15.3	89	18.7	53	18.8
269	13.3	303	15.7	85	21.2	53	17.0

The variations in the readings shown in this table are doubtless wholly due to variations in the electrometer leak; at least when this source of error was eliminated in the manner described the values checked as shown in Table I. It would thus appear that there is no temperature effect on aluminium when the temperature is raised as high as 340° C. The bulb containing this disk went through a long series of heatings as high as 500° C. while the pump was kept running; an induction coil was run intermittently on the tube at the same time; this was carried on for at least ten days or two weeks before any observations were made. This possibly accounts for the fact that so high a temperature was reached before any discharge due to the heat was present; the large bulb with which the present observations were made could not be con-

veniently sparked with a coil ; neither could it be heated as high as 400° C. except for periods of short duration.

On a separate bulb containing a small aluminium disk very consistent results were able to be secured to as high a temperature as 195° C. showing no increased discharge due to the temperature of the metal. This tube could be heated much hotter and the temperature was held at about 500° C. until no more gas appeared at the pump ; in general, it was noticed that the more the tube was heated while the pump was kept running and the more the coil was used on the tube, the more consistent were the results and the higher the temperature that could be reached before the heat discharge influenced the results.

The relative values of the discharging powers of the different metals follows none of the ordinary series of metals ; in general, it somewhat closely coincides with the melting point series, and yet it is hardly probable that the two phenomena have any necessary connection.

The following table showing the melting points of the metals and their order in the photo-electric series as determined in this investigation is inserted for comparison. The melting points are taken from J. Castell-Evans' physico-chemical tables and are those given by the author as the most probable values.

TABLE III.

Metal.	Melting Point.	Discharge Rate.
Cu.....	1050° C.	25.10
Au.....	1050	24.70
Ni.....	1450	24.00
Brass.....	—	23.80
Ag.....	968	17.16
Fe.....	—	16.40
Al.....	625	14.90
Mg.....	750	11.00
Sb.....	632	4.00
Zn.....	433	1.20
Pb.....	326	.90

Elster and Geitel arrange the metals of lower melting points in a similar series with reference to their power of discharging negative electricity in which just the opposite is shown, namely, the

lower the melting point the higher the value for the discharging effect. The following is their series to which has been attached the melting points.

TABLE IV.

Metal.	Melting Point.	Metal.	Melting Point.
Ru	38.5° C.	Li	180° C.
K	62	Mg	750
K + Na	—	Th	294
Na	97	Zn	433

IV. INFLUENCE OF TEMPERATURE UPON THE POSITIVE POTENTIALS ASSUMED BY THE DIFFERENT METALS.

In obtaining the positive potentials assumed by the different metals when exposed to ultra-violet light, the wire gauze and the metal cylinder were connected to earth; the wheel and its attached pair of quadrants were kept at zero potential, and the shutter in the screen, before the quartz window, was kept closed until an observation was ready to be made. Then the earth was removed from the electrometer and later the shutter was raised and the light kept on until the needle assumed a steady position. The time required for the needle to come to a permanent deflection varied with the different metals. If the source of light was placed farther away the time was longer but the final position of the needle was the same. Also, if the capacity was changed so as to alter the nature of the spark there was only a variation in the time necessary for the metal to assume this same potential. The average time necessary for the metals to assume the potentials given below was about 90 seconds; while at the same time one was unable to detect any leak in the electrometer over a period of five or six minutes. The values of the deflections could be repeated again and again to within less than one per cent. with those metals which assumed the higher potentials, the error being greater for the metals of lower potentials. That these readings were able to be duplicated to within so much smaller per cent. of error than in the previous set of observations on the rate of leak (Table I.) is probably due to the fact that in the observations on rate of leak the light was acting upon the metal for a comparatively short time, and might be less effective during one

ten-second interval than during another equal interval; while in this potential series, if the light was less effective during the first part of the period it would assume its normal value before the close of its period.

For the lower values of the temperature the readings could be made very accurately, but as soon as the discharge of electricity due to the heated condition of the metal was at all apparent, the potentials were reduced. The values of the potentials were checked up to about 100°C. and no increase was noticeable. The agreement between the different values of the potential (shown in Table V.) at different temperatures was of a somewhat higher order of accuracy than that shown in Table I. on the values of the discharge effect.

TABLE V.

Metal.	Deflection.					
	26°	40°	55°	60°	80°	95°
Ag	47.6	47.6	47.7	47.5	47.5	47.3
Fe	43.5	43.4	43.4	43.7	43.2	43.2
Au	43.1	43.2	43.1	43.0	43.1	43.0
Brass.	41.7	41.6	41.8	41.7	41.8	41.9
Cu	40.3	41.2	41.1	41.0	41.0	40.9
Ni	40.0	40.0	40.1	40.1	39.8	40.1
Mg	29.8	29.9	29.9	30.0	29.7	29.9
Al	26.2	26.2	26.2	26.1	26.3	26.2
Sb	14.0	14.1	14.0	14.1	14.1	14.0
Zn	7.0	7.0	7.1	6.9	6.8	6.7
Pb	00.0	00.0	00.0	0.00	00.0	00.0

Zeleny,¹ in his investigation on the effect of temperature upon platinum and iron exposed to ultra-violet light and surrounded by air at atmospheric pressure, observed a peculiar hysteresis effect, the discharges being greater when the metals were cooling than when they were rising in temperature. That particular effect was not noticed in these observations but a somewhat similar effect was observed; namely, that observations could be made at 50° to 60° higher when the temperature was rising than when it was falling. That is, if in the potential series 95° C. was the highest temperature at which good results could be obtained when the temperature was

¹ Zeleny, PHYSICAL REVIEW, Vol. 12, p. 321, 1901.

rising and if then the temperature was increased to say, 200° C., and the apparatus left to cool, then the first value that the heat discharge did not mask would be at about 40° or 30° C.

I desire to take this opportunity of acknowledging my obligations to Professors Michelson and Millikan for continued suggestions and assistance throughout this investigation, a considerable portion of which has been conducted in collaboration with the latter.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO,
September 1, 1906.

TEMPERATURE CONTROL OF THE CHELTENHAM MAGNETIC OBSERVATORY U. S. COAST AND GEODETIC SURVEY.¹

By J. E. BURBANK.²

A FULL description of the Cheltenham Magnetic Observatory is contained in the Annual Report of the Superintendent of the Coast and Geodetic survey for the year 1902, Appendix No. 5.³

The survey had maintained a magnetic observatory at Los Angeles, California, from 1882 to 1889 and also at San Antonio, Texas, during the period 1892 to 1895. In addition to the experience already gained a careful study was made of the best known foreign observatories and the methods employed to control temperature changes in their variation buildings.

As a result of this study it was decided to build the Cheltenham Observatory entirely above ground and provide sufficient heat insulation to reduce the annual range of temperature inside to a reasonably small amount, such a building would furthermore be free from the excessively humid conditions present in an underground structure.

The observatory is essentially a building within a building, the

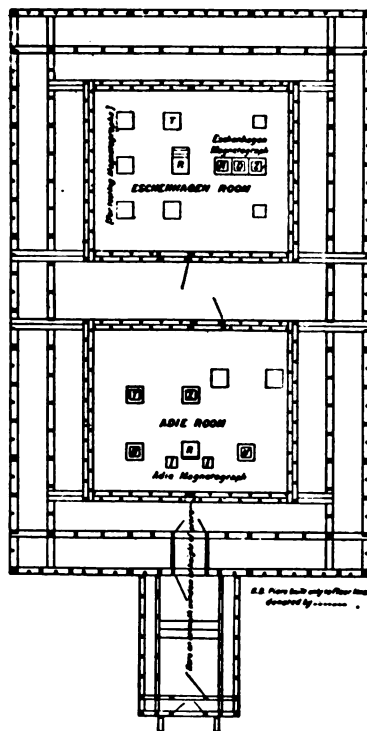


Fig. 1.

¹ Communicated with permission of the Superintendent Coast and Geodetic Survey.

² Observer in Charge of Cheltenham Magnetic Observatory.

³ See also Journal Terrestrial Magnetism, March, 1903, pp. 11-29.

inner portion being divided into two separate closed rooms known respectively, as the Adie and Eschenhagen rooms from the types of magnetographs which they contain. The walls of the outer building and also of the inner rooms are packed with dry pine sawdust.

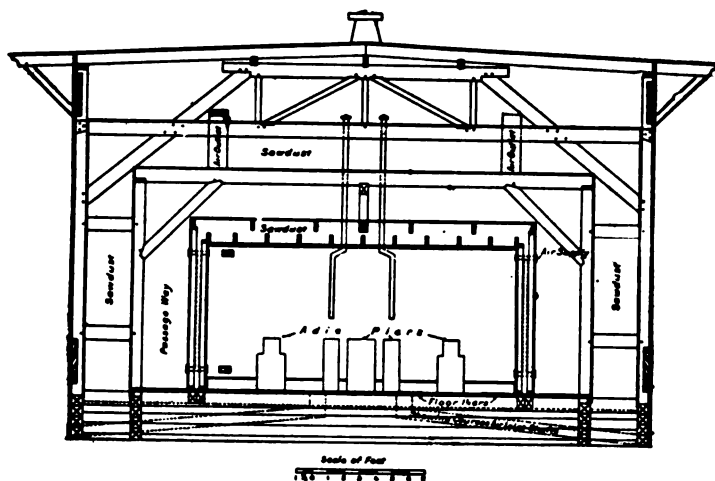


Fig. 2.

The wall thickness was designed to reduce the mean annual range of temperature, about 25° C. outside, to 4 or 5° C. inside, assuming no artificial heat and no openings in the walls for entrance or ventilation. For a plan of the variation building see Figs. 1 and 2.³

The inner rooms are each $19\frac{1}{2}$ by 16 by 9 feet inside measure and are entered through refrigerator pattern doors from a central corridor, $5\frac{1}{2}$ feet wide, extending between them, the sides and top are surrounded by an air space about 3 feet wide. In each room there are four small air shafts 3 inches square communicating with the air space around the rooms, these are fitted with slides and are generally kept closed. In the Adie room are three 3-inch ventilating tubes directly over the lamps and extending up into the attic, to carry off the hot air and products of combustion; during the winter these lamp ventilators are disconnected directly over the top of the room. A similar ventilator is provided in the Eschenhagen room. The doors, air shafts and lamp ventilators are the only openings in the inner rooms.

In the walls of the outer building there are four inlet shafts 5 by 10 inches and 16 feet long so placed that the air enters from the outside of the building near the ground and discharges through floor gratings into the passage-way at either end of the building. Four corresponding air outlet shafts 6 by 10 inches extend through the upper layer of sawdust into the attic. These air shafts are all provided with close fitting shutters and are opened only during the warm summer months. The outside wall has an 8-inch air space between the sawdust packing and the weatherboarding, connecting with the attic space, and provided with six ventilating windows, three on each side of the building near the ground ; during the hot weather these air shafts admit a cooling draft around the building during the night hours.

Entrance to the building is from the south side through a vestibule 10 feet by 13 feet 8 inches with walls containing two feet of sawdust packing. This vestibule is divided into three compartments, or air-locks, by four sets of close fitting doors.

The insulation of the building, beginning on the outside is : pine weatherboarding, 8-ply building paper, 1-inch pine sheathing, 8-inch air shaft, 1-inch pine sheathing, 8-ply paper, 3 feet pine sawdust, 8-ply paper, seven eighths inch pine ceiling, 3 feet 2 inches air space of passage-way, seven eighths inch pine ceiling, 8-ply paper, 1 foot pine sawdust, 8-ply paper, seven eighths inch pine ceiling. Beginning at the roof and going down the insulation is : gravel and pitch roof, three thickness tar paper, 1-inch pine sheathing, 3 feet 8 inches air space, 1-inch rough pine floor, 3 feet pine sawdust, 8-ply paper, seven eighths inch pine ceiling, 3 feet air space above rooms, 1-inch rough pine floor, 1 foot 6 inches sawdust, 8-ply paper, seven eighths inch pine ceiling, seven eighths inch pine floor, 8-ply paper, 1-inch pine under floor, 3 feet pine sawdust, 6-inch to 8-inch layer of gravel, 2 feet 8 inches of earth.

During the summer months, from about June 1 until October 15, the attic shutters are kept open so that a comparatively free circulation of air is obtained under the roof. During the night hours and on cool cloudy days the inlet shafts and the lower side shutters are opened allowing circulation of the air in the passage-way around the rooms and in the air shafts in the outside walls.

The Adie magnetograph consists of three photographic recording variometers each of which is lighted by a central draft student lamp. These lamps run continuously throughout the year, being kept as low as possible during the summer, they consume approximately $1\frac{1}{2}$ pints of common kerosene oil per 24 hours.

In the Eschenhagen room only one small lamp is used to light all three variometers. It uses approximately $\frac{1}{2}$ pint of oil in 24 hours. The presence of these lamps necessitates a temperature, in summer, considerably higher than the outside mean temperature, and in order to diminish the annual range it is necessary to maintain a correspondingly high temperature in winter. On account of the irregular nature of this source of heat any accurate control is out of the question, and it is not probable that any automatic device could be made to work satisfactorily.

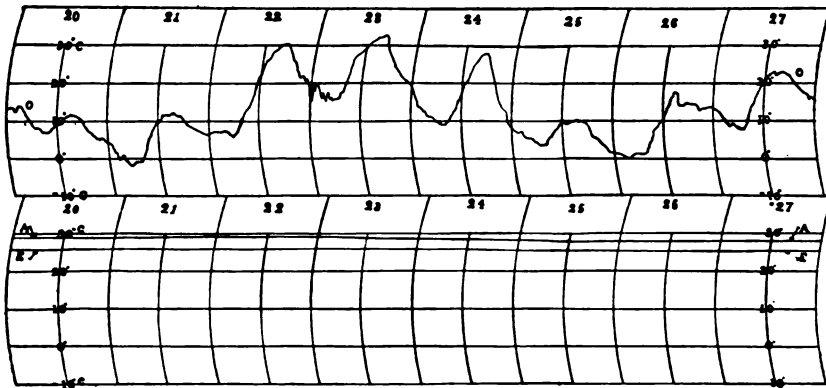


Fig. 3.

Thermograms Cheltenham Magnetic Observatory, March 20-27, 1907, O, Outside, A, Adie Room, E, Eschenhagen Room.

During the winter months additional lamps similar to the Adie lamps are used to heat the passage-way around the Eschenhagen room, in the coldest weather four or five are used continuously.

As a result of the past four years' record it has been shown that there is no diurnal variation, the occasional changes of one or more tenths of a degree being due to irregularities in the control of the heating lamps or ventilators. These irregularities are most common in the Adie room in the winter when the lamp ventilators are shut

off, at such times the change may amount to three or four tenths of a degree in a single night, due largely to irregularities in the Adie lamps. The changes in the Eschenhagen room rarely exceed one tenth of a degree in 24 hours.

It has been found that a temperature of about 28° C. in the Adie, and 25° C. in the Eschenhagen room, is best suited to present conditions.

It has been found repeatedly that a sudden change, amounting to 20° C. or 30° C. outside, can be entirely counteracted by the judicious use of heating lamps in winter and ventilators in summer, and in the case of long continued cold weather the effects are felt only gradually inside and need never amount to more than a few tenths of a degree.

As an example of the effect of a sudden change of temperature outside, see Fig. 3, which is copied from the thermograms obtained in the Adie room (*A*), in the Eschenhagen room (*E*), and outside (*O*), during the period March 20 to March 27, 1907. During this time there was an exceptionally large change of temperature, from -2° C. at 5 a. m. March 21, to 33° C. at 4 p. m. March 23, a change of 35° C. in 59 hours. The thermograph pen in the Eschenhagen room, which is normally four tenths of a degree higher than the instrument thermometers during this period, due to its setting when the sheet was changed, rose from 25.6° on March 20, to 25.9° on March 23, and fell to 25.4° on March 27. The rise was due largely to extra lamps used during ventilation of the passage-way on March 21. During the period March 24 to 27, when the effect of the hot wave should have been felt, the temperature inside the building was falling on account of the control of the heating lamps. In the Adie room the effect was similar but somewhat larger, there the decrease began on the 22d. In this particular instance the effect of the hot wave was overestimated and insufficient allowance was made for the low temperature of the sawdust packing.

In addition to a Richard thermograph in each room, each of the magnetic variometers is supplied with a thermometer and all of these thermometers are read daily at 8 a. m. and 4 p. m. From these readings, by aid of the thermograms, a table of hourly values is constructed, and from these hourly values the daily and monthly

mean values are derived. Since the declination results require no temperature corrections the mean of the temperatures of the two intensity variometers is taken as the magnetograph temperature.

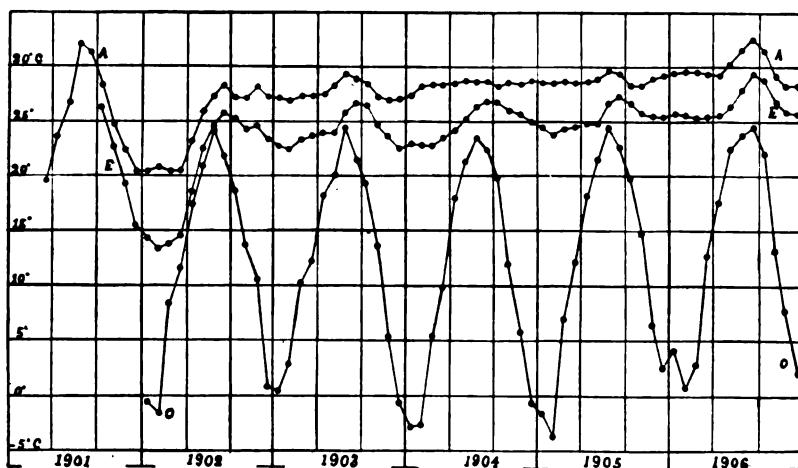


Fig. 4.

Monthly Mean Temperatures Cheltenham, Magnetic Observatory, 1901 to 1906. Adie Room (*A*), Eschenhagen Room (*E*), Outside (*O*).

In Fig. 4 are plotted the monthly mean temperatures, in degrees centigrade; of the Adie magnetograph (curve *A*), of the Eschenhagen magnetograph (curve *E*), and outside (curve *O*), from the beginning of each series of observations to the end of 1906. For the present comparison the monthly mean outside temperatures are derived from the daily maxima and minima. The mean derived in this way will doubtless differ somewhat from the monthly mean value of the hourly readings of the thermograms.

As will be noted the curves for the years 1901 and 1902 show that the method of temperature control was in the experimental stage and a comparatively large annual range was obtained. Beginning with 1903 a more careful control was exercised, especially over the Adie room which shows a much smaller annual range than the Eschenhagen. The curves also show a gradual upward tendency during the years 1905 and 1906, corresponding to the upward tendency of the outside temperature during those years. The lag of the inside temperature change over that outside is also shown in the case of the summer maxima in the Eschenhagen room.

The temperature ranges in degrees centigrade for the various years are given in the following table :

Annual Temperature Range in Degrees Centigrade.

	1902.	1903.	1904.	1905.	1906.
Adie room.	7.79	2.39	1.30	1.43	4.46
Eschenhagen room.	12.37	4.34	4.12	3.38	4.05
Outside (approximate).	26.00	25.00	26.00	28.00	23.70

Very little is yet known regarding the effect of changes of humidity on the quartz fibers supporting the Eschenhagen magnets, the effect of such changes on the silk fibers supporting the Adie magnets is undesirable. Beginning with 1902, observations of relative humidity have been made daily by means of a sling psychrometer, outside at 7:50 a. m., in the variation rooms between 8:10 and 8:20 a. m. The results show a slow but regular change inside the ob-

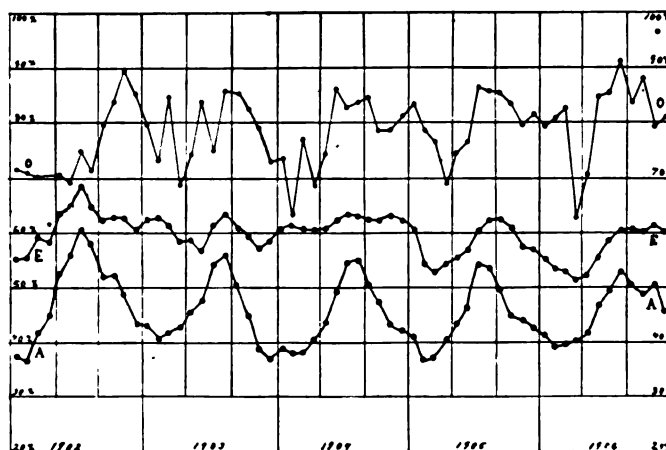


Fig. 5.

Monthly Mean Values of Relative Humidity, Cheltenham Magnetic Observatory, 1902 to 1906. Outside (O), Adie (A), Eschenhagen (E).

servatory with a maximum in summer and a minimum in winter, when the building is kept closed. The monthly range is seldom more than 2 or 3 per cent., while the annual range in the Adie room is about 15 to 18 per cent.

In Fig. 5 are plotted the monthly mean values of the relative

humidity, in per cent. for the Adie room (*A*), for the Eschenhagen room (*E*), and outside (*O*). The monthly mean of the relative humidity outside has no very great significance beyond showing the greater humidity in summer. It will be noted that the relative humidity in the Adie room is much lower than in the Eschenhagen due probably to the presence of the three lamps and the consequently dryer atmosphere. The higher humidity in summer is caused by the method of ventilating the building during cloudy days and during the night hours.

The total yearly consumption of oil at the observatory is approximately 300 gallons of which about 50 gallons is used in the absolute building, leaving about 250 gallons as the total amount used in heating and lighting the variation building. Of this 250 gallons, about 175 are used to illuminate the magnetographs, the remainder being used in the heating lamps in winter. This involves a total cost, for heat and light, of about \$25.00 per year.

THE EFFECT OF FREQUENCY UPON THE CAPACITY OF ABSOLUTE CONDENSERS.

BY J. G. COFFIN.

IT is proposed to construct an absolute air condenser of two circular plates of optically plane glass. Such plates cannot be easily made much larger than 10 cm. in diameter and hence must be placed very near to each other in order to obtain a sufficiently large capacity.

In order to render the two opposing faces of the plates conducting they are to be half-silvered so that light may be seen by transmission through them. They now form practically a Perot and Fabry interferometer¹ and the beautifully sharp fringes seen by transmitted light enable their parallelism and distance apart to be observed with the utmost accuracy at any instant. Knowing the geometrical dimensions of the system, its absolute electrostatic capacity can be calculated by means of a formula due to Kirchhoff,² in connection with certain edge-corrections worked out by the writer.³

The half-silvered conducting surfaces of the condenser, however, have a very high resistance, and a doubt arises as to whether this condenser is completely charged and discharged when a rapidly varying electromotive force is impressed upon it. The following calculations were undertaken in order to determine the amount of this effect.

RECTANGULAR PLATE CONDENSER.

As a first approximation consider the flow of electricity in a uniform strip of resistance R ohms per cm., and of capacity C farads per cm. (Fig. 1).

¹ *Théorie et Applications d'une nouvelle méthode de spectroscopie interférentielle*, Ann. de Phys. et de Ch., Vol. 16, p. 115, 1899. *Théorie des Franges des Lames Minces Argentées*, Vol. 12, pp. 459-501, 1897.

² Kirchhoff, *Gesam. Abhand.*

³ *Edge Corrections in the Calculation of the Absolute Capacity of Condensers*. P. A. A. S., Vol. 39, No. 19, Apr., 1904.

This represents a condenser made up of two insulated rectangular plates placed parallel to each other. The current enters at the edge AA' . The second plate is connected to earth.

Suppose an impressed alternating electromotive force,

$$V_0 e^{i\omega t}$$

where V_0 is the maximum E.M.F. and ω is the number of alternations in 2π secs., be impressed at one end of the strip.

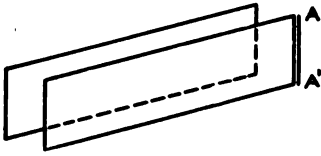


Fig. 1.

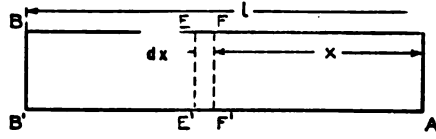


Fig. 2.

Consider an element of the strip of length dx at a distance x from the end AA' (Fig. 2). Let the current, which enters the element at FF' be denoted by I , then the current which leaves at EE' is $I + \partial I / \partial x dx$, and hence the rate of accumulation of electricity in the element dx is

$$I - \left(I + \frac{\partial I}{\partial x} dx \right) = - \frac{\partial I}{\partial x} dx = \frac{\partial}{\partial t} (dQ) = C \frac{\partial V}{\partial t} dx$$

because $dQ = C dx V$, where V is the potential at the element, so that

$$- \frac{\partial I}{\partial x} = C \frac{\partial V}{\partial t} \quad (1)$$

Similarly the difference in potential between the two edges of the element EF is

$$V - \left(V + \frac{\partial V}{\partial x} dx \right) = - \frac{\partial V}{\partial x} dx$$

which gives rise to a current of amount $IR dx$, so that :

$$IR = - \frac{\partial V}{\partial x} \quad (2)$$

We are here neglecting the E.M.F. due to self-inductance which in the cases here considered is *very* small in comparison with the large ohmic E.M.F. IR here assumed.

Eliminating I by differentiating equation (2) with respect to x , there results

$$\frac{\partial^2 V}{\partial x^2} = CR \frac{\partial V}{\partial t}. \quad (3)$$

Let the potential at any point of the strip be given by

$$V = V_0 f(x) e^{i\omega t} \quad (4)$$

where $f(x)$ is to be determined subject to the conditions that when

$$\begin{aligned} x = 0 \quad f(x) &= 1 \\ x = l \quad f'(x) &= 0 \quad (\text{equivalent to } \frac{\partial V}{\partial x} = 0). \end{aligned} \quad (5)$$

Substituting equation (4) in (3), there results a differential equation for $f(x)$

$$\frac{d^2 f(x)}{dx^2} = i\omega CR f(x) \quad (6)$$

which becomes if we write $-k^2 = i\omega CR$

$$\frac{d^2 f}{dx^2} + k^2 f = 0. \quad (7)$$

The complete solution of this equation is

$$f(x) = Ae^{ikx} + Be^{-ikx} \quad (8)$$

where A and B are the arbitrary constants.

Employing the boundary conditions (5), there results, for the determination of A and B , the equations

$$A + B = 1$$

$$Ae^{ikl} - Be^{-ikl} = 0$$

from which

$$A = \frac{e^{-ikl}}{e^{ikl} + e^{-ikl}} \quad B = \frac{e^{ikl}}{e^{ikl} + e^{-ikl}}$$

hence $f(x)$ is completely determined and

$$V = V_0 \left(\frac{e^{ik(l-x)} + e^{-ik(l-x)}}{e^{ikl} + e^{-ikl}} \right) e^{i\omega t}. \quad (9)$$

The total quantity of electricity in the condenser at any time is found by integrating $VCdx$ over the whole strip, thus :

$$\begin{aligned}
 Q(t) &= \int_0^l CV dx = CV_0 e^{i\omega t} \int_0^l f(x) dx \\
 &= \frac{CV_0 e^{i\omega t}}{ik} \frac{e^{ikh} - e^{-ikh}}{e^{ikh} + e^{-ikh}} = Q_0 e^{i\omega t} \text{ (say)}. \quad (10)
 \end{aligned}$$

We are principally interested in the maximum value of $Q(t)$, Q_0 , which is the coefficient of $e^{i\omega t}$ in the above equation. If the plates were good conductors this value of Q_0 would be ClV , hence the ratio of the apparent capacity (maximum) to its actual capacity for a steady charge is

$$\gamma = \frac{1}{ikh} \frac{e^{ikh} - e^{-ikh}}{e^{ikh} + e^{-ikh}} = \left[\frac{1}{kl} \frac{\sin(kl)}{\cos(kl)} \right], \quad (11)$$

γ is thus the number which tells us how much of the ordinarily assumed capacity is approached for any value of $k^2 = -i\omega CR$.

To realize the expression for γ which in k contains the $\sqrt{i}$ put

$$h(1+i) = ki.$$

In general the square of the absolute value of any imaginary expression (γ), is the product of it by its conjugate ($\bar{\gamma}$); the conjugate being obtained by replacing i wherever it occurs by $-i$, in the original expression. Hence

$$\begin{aligned}
 \bar{\gamma}\gamma = |\gamma|^2 &= \frac{1}{l(h+il)} \frac{e^{hl}e^{ihl} - e^{-hl}e^{-ihl}}{e^{hl}e^{ihl} + e^{-hl}e^{-ihl}} \times \frac{1}{l(h-il)} \frac{e^{hl}e^{-ihl} - e^{-hl}e^{ihl}}{e^{hl}e^{-ihl} + e^{-hl}e^{ihl}} \\
 &= \frac{1}{2h^2l^2} \frac{(e^{2hl} + e^{-2hl}) - (e^{i2hl} + e^{-i2hl})}{(e^{2hl} + e^{-2hl}) + (e^{i2hl} + e^{-i2hl})} \quad (12) \\
 &= \frac{2}{(2hl)^2} \frac{\cosh 2hl - \cos 2hl}{\cosh 2hl + \cos 2hl}
 \end{aligned}$$

Putting a single symbol λ for $2hl$, there results finally for $|\gamma|$ the expression

$$|\gamma| = \left(\frac{2}{\lambda^2} \frac{\cosh \lambda - \cos \lambda}{\cosh \lambda + \cos \lambda} \right)^{\frac{1}{2}} = \left(\frac{1}{\mu^2} \frac{\cosh \sqrt{2\mu} - \cos \sqrt{2\mu}}{\cosh \sqrt{2\mu} + \cos \sqrt{2\mu}} \right)^{\frac{1}{2}} \quad (13)$$

$$= \varphi_1(\mu),$$

where

$$\lambda^2 = 2(\omega CRl^2) = 2\mu^2$$

because $h(1+i) = ik$, $2ih^2 = -k^2$ hence

$$h^2 = \frac{-k^2}{2i} = \frac{i\omega CR}{2i} \text{ and } \lambda^2 = 4h^2l^2 = 2\omega CRl^2 \text{ and } \mu^2 = \omega CRl^2. \quad (14)$$

For large values of λ , γ clearly approaches zero, as $\cosh \lambda_{\lambda \rightarrow \infty} = \infty$ so that for this case

$$\gamma = \frac{1}{\sqrt{\omega CRl^2}} = \frac{1}{\mu}. \quad (15)$$

For $\lambda = 0$ the expression for γ is indeterminate, but its true value for small λ 's may be determined by expanding the functions $\cosh \lambda$ and $\cos \lambda$ in series and neglecting the higher powers of λ .

$$\begin{aligned} \gamma^2 &= \frac{2 \left(1 + \frac{\lambda^2}{2!} + \frac{\lambda^4}{4!} + \dots \right) - \left(1 - \frac{\lambda^2}{2!} + \frac{\lambda^4}{4!} - \dots \right)}{\left(1 + \frac{\lambda^2}{2!} + \frac{\lambda^4}{4!} \right) + \left(1 - \frac{\lambda^2}{2!} + \frac{\lambda^4}{4!} \right)} = \frac{2 \left(\frac{\lambda^2}{2!} + \frac{\lambda^6}{6!} \right)}{\lambda^2 \left(1 + \frac{\lambda^4}{4!} \right)} \\ &= \frac{1 + \frac{2\lambda^4}{6!}}{1 + \frac{\lambda^4}{4!}} = 1 + \frac{2\lambda^4}{6!} - \frac{\lambda^4}{4!} = 1 - \frac{28\lambda^4}{6!} = 1 - \frac{7}{45}\mu^4 = 1 - 0.156\mu^4. \end{aligned}$$

Finally, extracting the square root

$$|\gamma| = 1 - \frac{7}{90}\mu^4 = 1 - 0.078\mu^4. \quad (16)$$

Thus for $\mu = 0$, γ becomes unity, as of course it should. This equation is valid for values of μ less than unity.

In Fig. 5 is shown a plot of this function $\gamma = \varphi_1(\mu)$; φ_1 being explicitly given by equation (13).

CIRCULAR PLATE CONDENSER.

In order to obtain a solution for a *circular* plate condenser with an impressed E.M.F. $V_0 e^{i\omega t}$ at its rim a similar calculation follows. Instead of equation (11) we shall find a similar one with the trigonometric terms replaced by Bessel's functions.

As the lines of flow on account of symmetry are evidently radial, we may consider the case of an angular *strip* of length ρ cms.,

and 1 cm. wide at the larger end. (Fig. 3). Let R and C denote the resistance and capacity per unit length respectively, where the strip

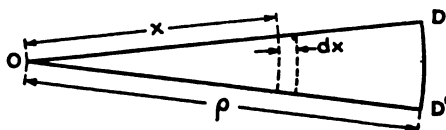


Fig. 3.

is 1 cm. wide. As we go out from the center O the capacity per unit length increases from zero at O to C at the rim $D D'$ while the resistance decreases from infinity at O to R at the rim.

The capacity per unit length at any point x of the strip is given by

$$c(x) = \frac{Cx}{\rho}.$$

The resistance is given similarly by

$$r(x) = \frac{R\rho}{x}.$$

Going through a similar demonstration to that for the rectangular plate condenser we find

$$-\frac{\partial I}{\partial x} = \frac{\partial}{\partial t}(dQ) = \frac{\partial}{\partial t}\left(\frac{VCx}{\rho} dx\right) = \frac{Cx}{\rho} \frac{\partial V}{\partial t} dx$$

so that

$$-\frac{\partial I}{\partial x} = \frac{Cx}{\rho} \frac{\partial V}{\partial t} \quad (17)$$

and

$$-\frac{\partial V}{\partial x} = \frac{R\rho}{x} I. \quad (18)$$

Differentiating equation (18) by x and making obvious substitutions there results for the differential equation satisfied by V in this case

$$\frac{\partial^2 V}{\partial x^2} + \frac{1}{x} \frac{\partial V}{\partial x} = CR \frac{\partial V}{\partial t}. \quad (19)$$

The conditions are, that when

$$x = \rho \quad V = V_0 e^{i\omega t},$$

$$x = 0 \quad \frac{\partial V}{\partial x} = 0 \quad (\text{condition for no current at the center}).$$

Assume that the potential at any point x is given by

$$V = V_0 e^{i\omega t} f(x),$$

where $f(x)$ is to be determined. Substituting this equation into the differential equation we find that $f(x)$ must satisfy the following one :

$$\frac{\partial^2 f}{\partial x^2} + \frac{1}{x} \frac{\partial f}{\partial x} + k^2 f = 0, \quad (20)$$

where $k^2 = -i\omega CR$, subject also to the conditions that when

$$\begin{aligned} x = \rho \quad f(x) &= 1, \\ x = 0 \quad f'(x) &= 0. \end{aligned} \quad (21)$$

The solution of (20) is

$$f(x) = AJ_0(kx) + BK_0(kx), \quad (22)$$

where J_0 and K_0 are the Bessels functions of order zero, of the first and second kinds respectively; and where A and B are the two arbitrary constants.

The conditions (21) give

$$\begin{aligned} 1 &= AJ_0(k\rho) + BK_0(k\rho), \\ 0 &= AJ'_0(0) + BK'_0(0), \end{aligned}$$

for the determination of the constants A and B .

As

$$J'_0(x) = \frac{\partial}{\partial x} J_0(x) = -J_1(x)$$

and $J_1(x)$ is zero when x is zero it follows that B is zero and hence

$$A = \frac{1}{J_0(k\rho)}$$

and

$$f(x) = \frac{J_0(kx)}{J_0(k\rho)},$$

so that finally :

$$V = V_0 e^{i\omega t} \frac{J_0(kx)}{J_0(k\rho)}. \quad (23)$$

This equation represents the potential V at any distance x from the center at any time t .

To find the quantity, $Q(t)$ of electricity upon the whole strip at any time we must integrate

$$dQ = VdC = V e^{kt} \frac{J_1(kx)}{J_0(k\rho)} \frac{Cx}{\rho} dx,$$

from one end of the strip to the other, obtaining

$$Q(t) = \frac{V e^{kt}}{J_0(k\rho)} \frac{C}{\rho} \int_0^\rho J_1(kx) \cdot x dx.$$

By means of the integration formula

$$\int_0^x u J_0(u) du = x J_1(x),$$

we obtain for $Q(t)$

$$Q(t) = \frac{V_0 C}{k} \frac{J_1(k\rho)}{J_0(k\rho)} e^{kt}. \quad (24)$$

We are particularly interested in the maximum quantity of electricity which is contained by the condenser. This quantity is the coefficient of e^{kt} in equation (24).

The quantity of electricity upon the strip, assuming the potential to be V_0 at all points is easily seen to be

$$Q_0 = \int_0^\rho \frac{V_0 C x}{\rho} dx = \frac{V_0 C \rho}{2}$$

so that just as in the preceding case we obtain for γ , the ratio of the apparent capacity to its capacity for a steady potential,

$$\gamma = \frac{V_0 C J_1(k\rho)}{k J_0(k\rho)} \bigg/ \frac{V_0 C \rho}{2} = \frac{2}{K\rho} \frac{J_1(k\rho)}{J_0(k\rho)}. \quad (25)$$

An instructive analogy may be observed between equations (11) and (25). The $J_1(x)$ being an odd alternating or periodic function somewhat similar to a damped harmonic sine function; while $J_0(x)$ is similar to a damped harmonic cosine function. An excellent graphical representation of the two functions $J_0(x)$ and $J_1(x)$ is to be found in Gray and Mathews, Bessel's Functions, page 292. Such analogies are to be looked for, and are a considerable help in proving the probable correctness of results.

It is shown¹ in works on Bessel's functions that

¹ Gray and Mathews, p. 156.

$$\frac{J_1(\eta)}{J_0(\eta)} = i$$

where η is a large imaginary quantity.

If we write

$$k^2 \rho^2 = -i\omega CR\rho^2 = -i\mu^2$$

then for large values of $k\rho$ or of μ

$$\gamma = \frac{2i}{\sqrt{-i\mu}} \text{ and its conjugate } \bar{\gamma} = \frac{-2i}{\sqrt{i\mu}}$$

Hence

$$|\gamma| = \frac{2}{\mu} = \frac{2}{\sqrt{\omega CR\rho^2}} \quad (26)$$

It is instructive to compare this last result with the equation which holds for large values of $\omega CRl^2 = \mu^2$ for the case of a uniform strip,

$$|\gamma| = \frac{1}{\mu} = \frac{1}{\sqrt{\omega CRl^2}}$$

these limiting equations hold for values of $\mu > 4$.

Thus for high frequencies the angular strip is *twice* as good as the uniform one.

That the angular strip would show less diminution in capacity for equal lengths could be seen *a priori*. Consider the two cases represented in Fig. 4. To form an angular strip from a uniform one,

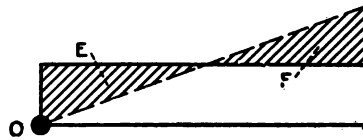


Fig. 4.

we take portion E , which is near the end and difficult for the electricity to reach and place it at F where the current may more easily fill it. The angular strip is thus evidently easier to charge than a corresponding uniform one of equal area and length. It is also easily understood that if the current be made to enter the angular strip at O that it will be theoretically impossible for any

charge to pass through the infinite resistance at the point o . This means practically that when a condenser plate is charged by a wire touching it at its center, that it is very difficult for the charge to spread from, or contract to, the point of contact. For this reason this case would involve far larger discrepancies for the rapid charging and discharging even, than the worst of the two worked out. The problem is theoretically capable of solution only on the assumption that the place where the current enters at o is a small but finite area. Such as the one indicated in the cut. These remarks indicate that such connections should be avoided.

For small frequencies ($\mu < 1$) we may obtain a simple expression for γ by expanding the J_0 and J_1 in series and neglecting all powers of the variable higher than the fourth.

Since

$$J_0(x) = 1 - \frac{x^2}{2^2} + \frac{x^4}{2^2 \cdot 4^2} - \frac{x^6}{2^2 \cdot 4^2 \cdot 6^2} + \dots$$

$$J_1(x) = \frac{x}{2} \left(1 - \frac{x^2}{2^2 \cdot 2} + \frac{x^4}{2^2 \cdot 4^2 \cdot 3} - \frac{x^6}{2^2 \cdot 4^2 \cdot 6^2 \cdot 4} + \dots \right)$$

$$\gamma = \frac{2J_1(x)}{xJ_0(x)} = \frac{1 - \frac{x^2}{8} + \frac{x^4}{192}}{1 - \frac{x^2}{4} + \frac{x^4}{64}} = \frac{\left(1 - \frac{\mu^4}{192}\right) + i\left(\frac{\mu^2}{8}\right)}{\left(1 - \frac{\mu^4}{64}\right) + i\left(\frac{\mu^2}{4}\right)}, \text{ if } x = \sqrt{-i\mu},$$

$$|\gamma|^2 = \frac{1 - \frac{\mu^4}{96} + \frac{\mu^4}{64}}{1 - \frac{\mu^4}{32} + \frac{\mu^4}{16}} = \frac{1 + \frac{\mu^4}{192}}{1 + \frac{\mu^4}{32}} = 1 - \frac{5}{192}\mu^4.$$

Hence

$$|\gamma| = 1 - \frac{5}{384}\mu^4 = 1 - 0.013\mu^4, \quad (27)$$

comparing this with the equation (16) for the uniform strip

$$|\gamma| = 1 - 0.078\mu^4$$

it is seen that the capacity of the angular strip falls off only about one sixth as fast as that of a uniform one, for very small frequencies.

In order to obtain the points for the intermediate frequencies it is necessary to employ the tables¹ for the values of

$$J_0(u\sqrt{i}) = X - Yi,$$

and were called by Lord Kelvin *Ber* (u) and *Bei* (u), meaning the real part and the imaginary part of the Bessels function respectively. The values of

$$J_1(u\sqrt{i}) = -\frac{\partial J_0(u\sqrt{i})}{\partial u} = -\frac{\partial X}{\partial u} + i\frac{\partial Y}{\partial u} = -X' + iY'$$

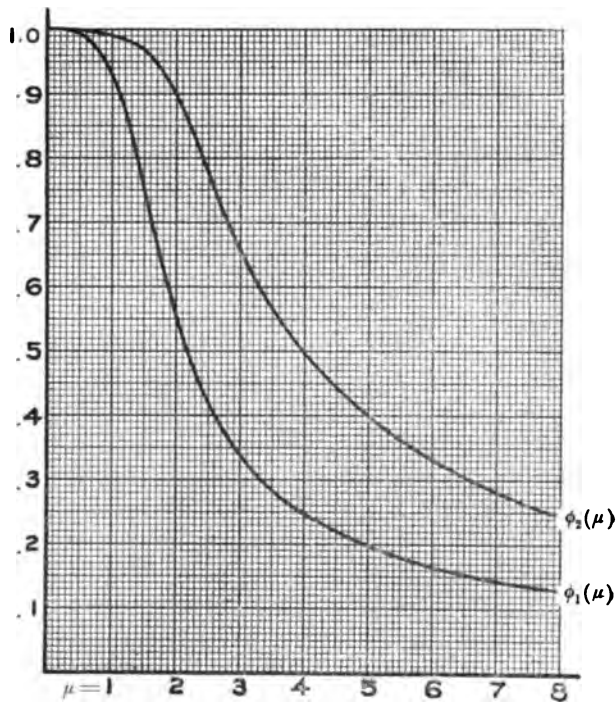


Fig. 5.

The plot shows graphically the two functions

$$\gamma = \phi_1(\mu) \text{ see equation (13) and } \gamma = \phi_2(\mu) \text{ see equation (28)}$$

for the rectangular and circular condensers respectively.

The ordinate, γ , is the fraction of the ordinarily assumed capacity to be used for any given value of the abscissa, μ .

For the rectangular condenser

$$\mu^2 = \omega CRl^2;$$

for the circular condenser

$$\mu^2 = \omega CR\rho^2$$

where ω , C , R , l and ρ have the same meaning as in the text.

¹ X and Y are tabulated on page 281 of Gray and Mathews.

were deduced from the table by the method of differences. Accordingly, if $\bar{\gamma}$ denotes the conjugate to γ we have

$$\gamma = \frac{2}{\sqrt{-i\mu}} \frac{-X' + iY'}{X - iY}, \quad \bar{\gamma} = \frac{2}{\sqrt{i\mu}} \frac{-X' - iY'}{X + iY},$$

and

$$\bar{\gamma}\gamma = |\gamma|^2 = \frac{4}{\mu^2} \frac{X'^2(\mu) + Y'^2(\mu)}{X^2(\mu) + Y^2(\mu)} = [\varphi_2(\mu)]^2. \quad (28)$$

A plot has been made of the two functions $\gamma = \varphi_1(\mu)$ and $\gamma = \varphi_2(\mu)$ for the two cases represented explicitly by equations (13) and (28) respectively. With any given R , C , l or ρ to every value of $\omega = 2\pi n$ corresponds a definite μ . From the curve the ratio of the apparent capacity (maximum) to the ordinarily assumed capacity (zero frequency) may be easily read off. It is graphically shown in the plot how rapidly the diminution of the acting capacity takes

Table Showing Decrease in Capacity of Condensers with Frequency.

n	μ	μ^2	μ^4	$\gamma = \phi_1(\mu)$	Decrease.	$\gamma = \phi_2(\mu)$	Decrease.
100	—	0.035	0.00122	.999	0.1%	.9998	.02 %
1,000	—	0.35	0.122	.99	1	.999	.1
10,000	1.87	3.5	—	.61	39	.925	7.5
20,000	2.64	7.0	—	.39	61	.75	25.0
40,000	3.74	14.0	—	.27	73	.53	47
Greater.				$\downarrow$ $= 1/\mu$		$\downarrow$ $= 2/\mu$	

place, especially after μ is slightly greater than 1.5 and how necessary it is in order to obtain reliable results to assure oneself that the correction is negligible or in case it is not, to carefully apply it.

In order to show how large these corrections may become in a definite case, we shall assume the following values for the constants, C , R , l and ρ . These values are of the order of magnitude that would occur with a half-silvered glass plate condenser, with the plates placed very close together.

$$R = 5,000 \text{ ohms per cm.}$$

$$C = 100 \text{ cms. per cm.} = \frac{100}{9 \times 10^{11}} \text{ farads per cm.}$$

$$l = \rho = 10 \text{ cms.}$$

$$\omega = 2\pi n.$$

Hence in this case

$$\mu^2 = \omega CRl^2 = \frac{100}{9 \times 10^{11}} \times 5,000 \times 100 \times 2\pi n = \frac{35}{10^3} n. \quad (29)$$

The results of this paper in connection with those on "The Effect of Frequency on Self-Inductance"¹ may serve to explain the observed deviations from the equation

$$T = 2\pi \sqrt{LC}$$

in past experimental work of this kind, as it is shown in these papers that *both* L and C tend to diminish in value with increasing frequency. This remark applies all the more forcibly, to work in which high frequencies are employed, such as wireless telegraphy.

RÉSUMÉ AND CONCLUSIONS.

The calculations of this paper were undertaken in order to find out how completely a condenser is charged and discharged when the condenser surface has a high resistance such as silvered glass, tin-foil, etc. The calculations are however perfectly general.

In order to attack the problem mathematically it was necessary to assume the simple case of a uniform strip and that of an angular strip, this latter corresponding to a circular plate condenser. The results show that when the surface resistance is high, that the capacity falls off to an enormous extent for comparatively low frequencies. A plot showing the ratio (γ) of the apparent acting capacity to the ordinary capacity has been made for both cases so that for any value of $\mu^2 = \omega CRl^2$ or $\omega CR\rho^2$, we may read off the corresponding values of γ , where C , R , and l or ρ may have any values whatever. The solution for the uniform strip is also one for a cylindrical condenser in which the current enters at one end; as the lines of flow are evidently along the generators. It has been found here that the capacity of a condenser diminishes with increasing frequency as well as the self-inductance of a coil; so that their effects are additive and in all work in which high frequency currents are employed, the experimenter must assure himself that the corrections pointed out are negligible for the work in question, and if not, to apply them.

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¹ The Influence of Frequency upon the Self-inductance of Cylindrical Coils of m -Layers. PHYSICAL REVIEW, Vol. XXIII., No. 3, September, 1906, and Bull. Bureau of Standards, Vol. 2, No. 2.

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INFLUENCE OF ATOMIC WEIGHT UPON THE MAXIMA OF ABSORPTION AND REFLECTION BANDS.¹

BY W. W. COBLENTZ.

FROM various considerations one would expect to find the position of the maxima of the bands of selective absorption and of selective reflection, which are characteristics of certain groups of atoms, to be affected by the molecular weight of the compound. Heretofore the evidence has been more or less contradictory. The difficulty lies in the interpretation of the results. Previous experiments have failed to show a shift of the band with increase in the number groups of atoms in the molecule. This is hardly to be expected if the *cause* of the bands is to be attributed to groups of atoms. On the other hand, the *position* of the band has finally been shown to depend upon the atomic weight of the element (metal) with which group of atoms is combined to form a compound. A recent study of the reflection bands of the sulphates of (H₂, Mg, Ca, Sr, Ba) SO₄, which have a series of reflection bands from 8.2 to 9.4 μ , and of the carbonates of (Mg, Ca, Fe, Cu, Zn, Sr, Ba, Pb) CO₃, which have a complex double band at 6.5 to 7.2 μ , shows conclusively that the maximum of the band shifts toward the long wave-lengths with increase in the atomic weight of the metal, and confirms the writer's previous work on transmission and reflection spectra. In the carbonates the first reflection band shifts from Mg 6.5 μ , Ca 6.58 μ , Fe 6.62 μ , Zn 6.64 μ , Sr 6.72 μ (band not resolved), Ba 6.8 μ , to Pb at 6.94 μ ; the second band shifts from Mg 6.86 μ , Ca 6.9 μ ; Fe 7.0 μ (?), Zn 6.92 μ , Ba 7.0 μ , to Pb at 7.18 μ .

In the sulphates the first reflection band shifts from Sr at 8.2 μ to Ba at 8.31 μ ; the second band shifts from H₂ at 8.62 μ , Mg 8.65 μ , Ca 8.69 μ , Sr 8.78 μ to Ba at 8.87 μ ; the third band shifts from K at 9 μ , Sr 9.05 μ , to Ba at 9.11 μ ; the fourth band shifts from Sr at 9.28 μ to Ba at 9.35 μ .

In the transmission bands of these sulphates the first band shifts from Mg at 4.53 μ to Ba at 4.62 μ ; the second band shifts from Mg at 6.1 μ ,

¹ Abstract of a paper presented at the Washington meeting of the Physical Society April 19-20, 1906.

Ca at 6.15μ to Pb at 6.4μ ; the third band shifts from Ca 6.54μ to Pb at 6.75μ , and are additional evidence that the position of the maximum of the band depends upon the atomic weight of the element (metal) with which the group of atoms is combined.

AN ACCURATE CALORIMETER.¹

BY WALTER P. WHITE.

THIS calorimeter is used in connection with an electric resistance furnace. It is therefore completely enclosed with a double-walled jacket through which water is kept circulating. As the amount of manipulation necessitates the maximum simplicity in methods of measurement, the temperature is determined by a thermo-element, which can be read on a potentiometer almost at the same time with the temperature of the furnace, the differential temperature of the calorimeter and jacket, and the voltage and current used in calibration. The temperatures can be read concordantly to about $.001^\circ$. The use of large calorimeters and small temperature intervals has been recommended in order to reduce cooling corrections, but at best a small gain in cooling correction, when secured in this way; requires a very large increase in the sensitiveness of the thermometer, while in so far as the cooling errors come from the difficulty of *determining* the cooling correction or from the heat generated in stirring, they are actually greater in the large calorimeter. Hence the temperature interval of 20° was chosen.

Evaporation has been rendered negligible by floating the cover upon the water. The calorimeter resembles in plan a figure eight with a propeller in one side. Dead spaces are thus completely avoided.

Further reasons for a small temperature interval and large calorimeter are found in the closer approximation to Newton's law of cooling and in the reduced effect of the metal parts of the calorimeter. With the present arrangement of jacket and floating cover, however, practically everything within the case is at one of two temperatures, that of the calorimeter water and that of the jacket water, whose difference is accurately measured. Uncertain and lagging temperatures of the metal parts are thus practically eliminated. The slight variation from Newton's law is easily determined and applied as a correction, since the difference in temperature between the calorimeter and its *whole* environment can be at all times exactly known.

Experience has shown that the regularity of the cooling is at least equal to the maximum accuracy obtained in measuring it. The prin-

¹ Abstract of a paper presented at the Washington meeting of the Physical Society April 19-20, 1907.

cial errors thus far observed have been clearly traceable to lack of sensitiveness in temperature measurement. The selection of a wide temperature interval, therefore, seems completely justified.

Calibrations by the electrical method are still in progress. Seven preliminary results with inferior sensitiveness have already shown an average variation of only two parts in 10,000.

ON THE MEASUREMENT OF THE INTENSITY AND DAMPING OF HERTZIAN WAVES IN AIR.¹

BY WALTER P. WHITE.

FOR quantitative work in this subject, a thermoelement or bolometer seems necessary. Enclosure in a vacuum is of great assistance, and a fine platinum wire bolometer can be so enclosed much more compactly than a thermoelement. It is also capable of considerably greater sensitiveness than the element. With 30 cm. waves at a distance of 2 m., and a moving coil galvanometer of 2.6 seconds full period, a sensitiveness of 6,000 scale divisions was attained. In spite of this combination of quickness and sensitiveness, the apparatus was very convenient to work with. Working at night, and many other precautions taken by previous observers, were entirely unnecessary.

The bolometer wire was, in the most sensitive arrangement, of platinum, 2.2μ in diameter, 5 mm. long, with a resistance of 100 ohms. This size of wire was found comparatively easy to handle. The wire was heated 34° by the strongest oscillations. It is mainly owing to the possibility of using finer wire, with a consequent increase in the heating, that the bolometer excels the thermoelement in sensitiveness.

To eliminate variations in intensity a comparison receiver was balanced (by varying its plane of polarization) against the principal receiver, using the galvanometer as a null instrument, and readings agreed to .1 per cent. Very slow variations in the ratio of the two receivers amounting to 2 per cent. sometimes occurred, due possibly to changes in the damping from variations in the spark. Long electrolytic leads between induction coil and oscillator largely eliminated disturbing vibrations and increased the intensity. The induction coil was used on alternating circuit as a transformer, and at least 60 sparks (in kerosene) passed per alternation.

The bolometer lends itself especially well to the production of a sensitive receiver of high damping, which will do much of the work of the long-desired indifferent receiver. By running interference curves and varying the effective intensity of one of the interfering wave trains

¹ Abstract of a paper presented at the Washington meeting of the Physical Society, April 19-20, 1907.

(by changing its plane of polarization by rotating a grating mirror), the effect of one, two, three, or more waves can be isolated. The law of damping may thus be determined. The highly damped receiver proved sufficiently sensitive for this kind of work, but accurate results were prevented by the oscillations reflected from the iron pipes in the room.

An attempt to use a mercury interrupter for these short oscillations was unsuccessful.

THE EFFECT OF THE TIME OF PASSAGE OF A QUANTITY OF ELECTRICITY ON THE THROW OF A BALLISTIC GALVANOMETER.¹

BY F. WENNER.

THE case considered is that of the throw produced when a ballistic galvanometer is connected in series with a condenser and the condenser charged. The galvanometer is of the moving coil type with a radial field and the motion is undamped.

The charging current is represented by the equation,

$$i = Q \frac{a_1 a_2}{a_1 - a_2} [e^{-a_1 t} - e^{-a_2 t}]$$

where

$$a_1 = \frac{R}{2L} + \sqrt{\frac{K^2}{4L^2} - \frac{1}{CL}} \text{ and } a_2 = \frac{R}{2L} - \sqrt{\frac{K^2}{4L^2} - \frac{1}{CL}}$$

The moments acting on the coil equated to zero give,

$$I \frac{d^2 \phi}{dt^2} + \beta \phi = Gi.$$

Substituting the value of the current from the first equation, integrating and making use of well known relations give, when the charge occurs in a time less than the quarter period of the coil and the self inductance is small,

$$Q = \frac{aT}{c2\pi} \cdot \operatorname{cosec} \left[\tan^{-1} \frac{T}{2\pi CR} \right] \phi \cdot (\text{approximately}).$$

This equation shows that the time of charge, which depends on the resistance and the capacity, has but little effect unless the product of the resistance and capacity is large or the period of the coil is small.

Experiments with large capacities and variations of the resistance sufficient to change the throw twenty per cent. gave results in fair accord with those calculated from the equation.

The following is the notation used:

I = the moment of inertia of the coil,

¹ Abstract of a paper presented at the Washington meeting of the Physical Society, April 19-20, 1907.

φ = the angular displacement of the coil,
 t = time,
 β = the torsional moment of the suspensions,
 G = the coil and field constant,
 i = the current during charge,
 Q = the charge or quantity,
 L = the coefficient of self inductance,
 C = the capacity of the condenser,
 T = the period of the coil,
 a = the steady deflection of the coil,
 c = the current producing the steady deflection of the coil,
 ϕ = the throw of the coil.

A REDETERMINATION OF THE WAVE-LENGTHS OF THE IRON LINES.¹

BY A. H. PFUND.

AS the work of Michelson and Kayser has shown that not only Rowland's values but Rowland's method of determining wave-lengths are faulty it has been decided by the International Union for Coöperation in Solar Research that a redetermination of the wave-lengths of standard lines be carried out according to the interference method of Fabry and Perot. In order to test this method thoroughly it was agreed upon that several investigators, working independently, carry out determinations on the same (iron) lines, and it was with the object of performing a portion of this work that the present investigation was undertaken.

The method used differs from that of Fabry and Perot only in details: the interferometer plates are kept in a constant temperature enclosure which does not vary by one-twentieth degree centigrade for several weeks; then again the entire Fabry and Perot ring system is projected on the slit of a spectroscope which is so arranged that in its focal plane the spectral lines and the ring system are simultaneously brought to a focus. Each line has superimposed upon it a portion of its ring system and thus results for all of the iron lines are obtainable at a single exposure.

The measurements thus far made agree with those of Fabry and Perot to within less than one part in a million. It is intended to carry out determinations of equal accuracy on the lines of titanium which are far superior, as standards, to the lines of iron.

JOHNS HOPKINS UNIVERSITY,
April, 1907.

¹ Abstract of a paper presented at the Washington meeting of the Physical Society, April 19-20, 1907.

FINDING DIRECTION BY MEANS OF SUBMARINE SOUND SIGNALS.

BY LUCIEN IRA BLAKE.

ONE of the methods at present employed by the Submarine Signal Company of Boston for locating the source of a submarine sound signal is to attach two iron tanks, one to the port — the other to the star-board wall, inside a vessel below the water line and toward the bow. In each of these tanks, filled with water, is suspended a microphonic transmitter which is connected through a port and starboard indicator box to a receiving telephone in the pilot house. According to the ship's course, the different intensities of the sounds received locate the direction of the sound source. In every day practice this is successfully done to within a half of a point, and on about 160 vessels at present, among which are the largest trans-Atlantic steamers. The generally accepted hypothesis that a vessel in the path of a submarine sound casts an acoustic shadow has been used to explain this difference in intensity. It is to be observed, however, that marked differences in intensity occur on the *exposed* side of the vessel, where no shadow exists. The sound is louder when the source is abeam than in any other position. Further, there are decided differences in the *quality* of the sound delivered into the two tanks — even when one is in the alleged shadow. This difference in quality, although with the majority of observers unconsciously perceived, is, I believe, a larger factor in determining sound direction than intensity, and is not explainable on a geometric shadow principle. It would therefore seem necessary to look for some other principle than simple acoustic shadows. So far as variations in intensity are concerned, these can be produced from a cause which is not only amenable to mathematical analysis, but also to experimental demonstration.

From an article by Green, "On the Reflection and Refraction of Sound," Cambridge Transactions, 1838, it is possible to derive two equations, one for the reflected and one for the refracted wave, in terms of a velocity potential. Let φ and φ_1 represent the velocity potentials respectively. Then,

$$\varphi \text{ (reflected)} = \frac{\frac{\rho_1 - \cot \theta_1}{\rho} - \frac{\cot \theta}{\rho_1 + \cot \theta}}{\frac{\rho_1 - \cot \theta_1}{\rho} + \frac{\cot \theta}{\rho_1 + \cot \theta}} \left[\cos \frac{2\pi}{\lambda} (-x \cos \theta + y \sin \theta + \nu t) \right]^{\frac{1}{2}},$$

$$\varphi \text{ (refracted)} = \frac{2}{\frac{\rho_1 - \cot \theta_1}{\rho} + \frac{\cot \theta}{\rho_1 + \cot \theta}} \left[\cos \frac{2\pi}{\lambda} (x \cos \theta_1 + y \sin \theta_1 + \nu_1 t) \right]^{\frac{1}{2}},$$

ρ, ρ_1 represent densities; θ and θ_1 angles of incidence and refraction.

In the expression for the amplitude of vibration of the refracted sound,

$$\left(\text{viz., } \frac{2}{\frac{\rho_1}{\rho} + \frac{\cot \theta_1}{\cot \theta}} \right),$$

$$\frac{\cot \theta_1}{\cot \theta} = \frac{\nu}{\nu_1} \left[1 - \left(\frac{\nu_1^2}{\nu^2} - 1 \right) \lg^2 \theta \right]^{\frac{1}{2}}.$$

Whence the intensity of the refracted sound is proportional to

$$\frac{2}{\frac{\rho_1}{\rho} + \frac{\nu}{\nu_1} \left[1 - \left(\frac{\nu_1^2}{\nu^2} - 1 \right) \lg^2 \theta \right]^{\frac{1}{2}}},$$

or depends simply upon the angle θ at which the sound strikes the side of the vessel.

From the above analysis, it is easy to see that, as far as intensity is the factor, direction finding by submarine sound signals must depend upon the angles at which the sound enters the side of a ship—and as (except when the sound is dead ahead or astern) the angles presented by the two sides to the direction of the sound are *different*, the intensities of the two sounds are different in the two receiving tanks and thus the transmitters submerged in these tanks indicate different intensities—the louder on the side where the incident angle is the smaller; that is, on the side toward the sound.

In this analysis it is premised that no sound shadow therefore exists on the remote side of the vessel, but that the sound bends around the vessel as an obstacle, and thus enters the portions of the remote side at angles different from the incident angles of the exposed side. It is easy to calculate how far this assumption may be carried out and what influence it has upon direction finding. It is well known that for long waves impinging upon an obstacle diffraction bands are pronounced and rays of sound for long waves cannot be considered to exist. We can, therefore, calculate how much sound of a given pitch bends around a vessel to enter its remote side, and also the distribution of the diffraction bands on that side. This will lead us to an explanation of the different *quality* of the tones, also of what effect the side of the vessel had and of the effect of the distance of the sound. It gives also a clue as to the best location of the receiving tanks.

A rigid surface, in order to reflect a sound and thereby to produce a shadow back of it, must intercept say at least ten Huyghen's zones. The radius of the n th zone will be obtained from the formula

$$r^2 = \frac{n\lambda}{\frac{1}{R} + \frac{1}{C}}.$$

- r = radius of Huyghen's half period zone,
 R = radius of curvature of the wave front at the side of the vessel,
 C = distance from wave front to the point where the intensity is desired,
 λ = wave-lengths,
 n = an integer.

It becomes thus a calculation of Huyghen's zones under given conditions of pitch, distance of the sound source and size of the vessel.

I give here for illustration some calculations based upon the pitch of the present standard lightship diaphragm striker of the Submarine Signal Company for a vessel at 5 miles distant from the striker in open sea. The pitch of the bell is $C''' = 1,215$ vs/sec. and the wave-length is therefore 3.9' at 60° F., which may be called 4'.

In applying this formula to any particular vessel, one half the breadth of beam is taken as equal to C .

For the Submarine Signal Company's steamer *Sabrina*, $C = 10$ feet approximately. The draft of the steamer is 7 feet.

$$r_{n=1} = 6.3 \text{ feet.}$$

At 5 miles

$$r_{n=10} = 20 \text{ feet.}$$

So that the diffraction bands would be about 2' apart from the bow with the first one covering 6'. It is therefore clear that maxima and minima of intensity would show from the bow aft, growing weaker and weaker for about 20'—when practically a real shadow would begin.

Taking into consideration, however, the draft of the boat, it is self-evident that the same type of bands of maximum and minimum intensity must start from the keel and extend upward parallel to it to about the same distance of 20' for the conditions stated. Thus the shadow which the length of the vessel might show would be obliterated by the bending of the sound up around the keel. It is clear, then, that a shadow could not be cast by a vessel for a 4' wave—unless the vessel was over 40 long and over 20' draft—and even then the shadow would begin 20' up from the keel.

THE INFLUENCE OF FREQUENCY ON THE RESISTANCE AND INDUCTANCE BY COILS.

BY LOUIS COHEN.

IT has been shown experimentally by several investigators that the change in resistance of a coil due to frequency is different from that of a straight wire of the same length as the winding of the coil. The difference arises from the fact that the distribution of the current in the

wire is different in the two cases. Professors Wien, Sommerfeld, and others have independently worked out the problem theoretically and derived certain formulas for the change in resistance. The results, however, obtained by the various investigators are not satisfactory, they do not agree with the experimental results.

In this paper the problem was considered from an entirely different standpoint, and very satisfactory results were obtained, in fact the results arrived at theoretically agree remarkably close with the experimental results obtained by Wien.

According to the theory developed in this paper, the increase in resistance is proportional to the radius of the coil, diameter of wire, pitch, frequency and conductivity of material winding. The final formula obtained is as follows :

$$R = 128s^2p^2\pi d\sigma \sum_{n=1}^{n=\infty} \frac{1}{n^2(a_n^2 + \beta_n^2)} a_n$$

where

THE PHYSICAL REVIEW.

HEAT OF EVAPORATION OF WATER.

BY ARTHUR WHITMORE SMITH.

INTRODUCTION.

THE amount of heat required to evaporate a gram of water at ordinary room temperatures is only approximately known, and this knowledge comes largely from determinations made at other temperatures. The familiar formula of Regnault certainly gives too large values as is shown by the more recent work of Griffiths and of Henning for the range 30° – 100° C., and of Dieterici at 0° C. The present investigation fills in the range 0° – 40° C. And the need of this determination is evident when one considers that during the past ten years there have been in progress in this country several elaborate investigations, costing tens of thousands of dollars, and in each of which the heat of evaporation of water at room temperatures is an essential factor. For want of better values those of Regnault are still used.

The evaporation of water at low temperatures can be accelerated in two ways. The method usually employed is to reduce the pressure until the water boils freely at the desired temperature. The other method, which has been tried by several investigators and discarded as unsatisfactory, is to pass a stream of dry air through the water. This air becomes saturated with water vapor and the amount of evaporation can be easily controlled by regulating the air current. While there are precautions which must be observed, there are also advantages in the latter method, for not only is the amount of evaporation always under control, but, what is more im-

portant, the temperature of the water can be held constant at the desired point for any length of time. Moreover the stirring is complete and thorough without introducing any of the uncertainties or corrections involved with a mechanical stirrer. The evaporation of water in nature is slow and quiet, and takes place into air at atmospheric pressure. Natural conditions are therefore more nearly approached by this method than by violent ebullition under reduced pressure, and with the arrangement described below it has proved entirely satisfactory.

PLAN OF THE INVESTIGATION.

The plan of this investigation is to draw dry air through the water within a suitable calorimeter, thereby causing it to evaporate, and by means of an electric current to supply the heat required for this evaporation. As a matter of fact the heating current was always maintained constant, while the current of dry air was continually adjusted to the value required to maintain the reading of the thermometer at the chosen point. In this way all of the heat supplied by the current was used in the evaporation of water, and none of it went to changing the temperature of the apparatus. Moreover, as the calorimeter was always kept at the temperature which it assumed of itself after standing two or three days surrounded by a constant temperature bath, there is also no radiation correction. All that it is necessary to know is the amount of heat supplied by the electric current, and the amount of water evaporated.

The former quantity is readily computed from the formula EIT . For determining the latter, the various forms of calorimeters were all designed with the intention of directly weighing them on a delicate balance, just before and immediately after each experiment. The loss in weight would give at once the amount of water evaporated. However desirable such an arrangement might be it was found that the thermal uncertainties introduced by removing the calorimeter from its constant temperature chamber were greater than any possible gain from the direct weighing. It therefore became necessary to determine the amount of water evaporated by collecting it from the air current after it had left the calorimeter. The air was taken from the room and passed through two H_2SO_4

tubes, a tube filled with absorbent cotton to catch any possible acid that might by any chance come over with the air, then through a meter of block tin pipe in the constant temperature bath, to the calorimeter. Leaving the calorimeter, the air current, now laden with its load of moisture, passed as directly as possible to two H_2SO_4 tubes and thence to the aspirator pump. All the water brought from the calorimeter is left in these last two tubes, and their gain in weight gives the amount of water evaporated.

ADVANTAGES OF THIS METHOD.

This method possesses several advantages over others that might have been used. The water is slowly evaporated into air at nearly atmospheric pressure and therefore corresponds more nearly to natural evaporation than when the water boils under reduced pressure. Besides water does not boil easily or steadily at these low temperatures. But the principal advantage is that an experiment can be commenced or ended at any time without disturbing the setup in the least, and one experiment can follow another with no interval between. When everything is running smoothly and well, a recently weighed pair of H_2SO_4 tubes can be inserted in the air circuit to collect the water vapor coming from the calorimeter, and the old tubes removed and weighed. Two hours later the tubes are changed again, and the collected water is that which has been evaporated by the heat supplied during the same period. Thus the experiment has neither starting nor stopping, with all the attending uncertainties and corrections.

THE CALORIMETER.

The final form of the calorimeter consisted of a large test tube, *E*, Fig. 1, closed at the top by a cork which was filled and covered with pure paraffin. Two glass tubes for the air current passed through this cork, one extending to the bottom of the test-tube, the other passing through only two centimeters. A third tube, closed at the lower end, and not shown in the figure contained the heating coil, a single heater from a Nernst lamp provided with current and potential terminals. No heat could escape up this tube as it was filled with beeswax the greater part of its length, which also served to support and insulate the four leading-in wires. The coil itself was

surrounded with kerosene, the better to conduct the heat to the surrounding water. A fourth tube of thin test-tube glass, also closed at the lower end and extending to the bottom of the calorimeter, contained the thermometer, *T*. Good thermal contact between the walls of the tube and the bulb of the thermometer was secured by means of a little mercury, sufficient to cover the latter. Thus the thermometer could be easily removed for comparisons and there was less chance of breakage, either of the thermometer or the calorimeter. These tubes were all sealed in at the top of the

calorimeter and outside the paraffined cork by means of "universal wax," which while affording little support does ensure an air-tight closure.

This test-tube calorimeter stood within a double walled Dewar vacuum tube, *D*, the whole being well surrounded with light cotton wool and held in a pasteboard box, which in turn was supported in the middle of the constant temperature chamber, *F*. The remaining space around the sides, the top and the bottom of this chamber was lightly filled with cotton wool to prevent convection air currents.

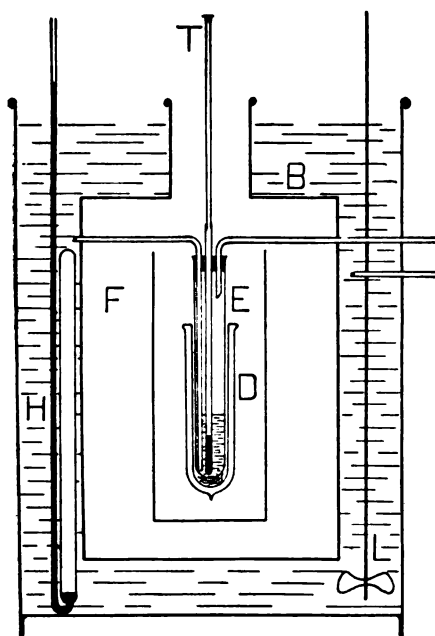


Fig. 1. The Calorimeter as arranged within the constant temperature water-bath.

The calorimeter was always packed thus thoroughly at

least as long as the day before an experiment was to be performed in order that the entire contents of the chamber might assume the temperature of the surrounding bath. Heat moves but slowly through this thorough packing, but complete thermal equilibrium is essential if the calorimeter is to lose or gain no heat by radiation, convection or conduction during an experiment.

THE WATER-BATH AND THERMOSTAT.

The constant temperature chamber was surrounded on all sides and nearly to the top of the neck by the constant temperature water bath, *B*. The temperature of this bath was maintained constant by an automatic gas thermostat, *H*, and the water was kept well stirred by a rotary stirrer, *L*, driven by a small electric motor. The final form of thermostat, and one which proved entirely satisfactory, consisted of a long glass bulb holding about one third of a liter, from the bottom of which the stem extended to above the surface of the water. Near the top of the stem it was drawn down to a small cross-section through which the mercury would rise or fall more rapidly than at other points where the tube was full size. The bulb was filled with alcohol for trial and as this proved satisfactory it was not exchanged for toluol. The stem, of course, was filled with mercury. Within the upper portion of the stem and extending down to the top of the mercury column was a smaller tube, ending in a fine point. Down this fine tube and up around it flows the gas for the burners under the bath. When the mercury rises it closes the end of this tube and thus shuts off the supply of gas. Much to my surprise this thermostat proved to be fully as sensitive at points where the stem was full size as at the more constricted portion. At the latter point the mercury rose rapidly, completely shutting off the supply of gas, save for the pilot light, and allowing the bath to cool — often far below the standard temperature. Where the tube was broader the mercury rose more slowly, shutting off the gas only partially and keeping a moderate, steady flame under the bath, just sufficient to maintain the constant temperature. In every way this thermostat did its work well, and it was not unusual for it to hold the bath constant to within one hundredth of a degree for a period of several consecutive days.

THE H_2SO_4 TUBES.

The tubes containing the acid were obtained from the chemical laboratory, and are known as gas wash bottles. In each were placed 50 c.c. of concentrated, chemically pure, sulfuric acid, density 1.84, filling it to a depth of about six centimeters. The air bubbled through this in four small streams, and only after several grams of

water had been caught did any appreciable amount pass through to the second tube. When this stage was reached the tube was refilled with fresh acid.

Although this furnished a convenient method for collecting the water from the air current, considerable difficulty was experienced in weighing the tubes. That is, the same tube standing idle would not give a constant weight when weighed several times during the day. It is not necessary to recount here the weeks spent in trying to eliminate this variation. The trouble seemed to be due to the condensed layer of moisture on the outside of the glass, and various schemes to reduce this were tried, such as using an atmosphere dried with sulfuric acid; wiping the tubes with a soft cloth and allowing them to stand a definite period before weighing, etc. Finally, by placing one H_2SO_4 tube on one balance pan and a

similar tube also filled with acid on the other pan, and treating them just alike between weighings, their difference was found to remain constant. No other counterpoise of brass or of glass would answer as well, and therefore with each pair of tubes was a third one through which no air ever passed, but which was otherwise treated precisely like the others, the three being kept together all the time whether in use or not. Of course they were all kept tightly closed from the air except the two when the air current was passing through

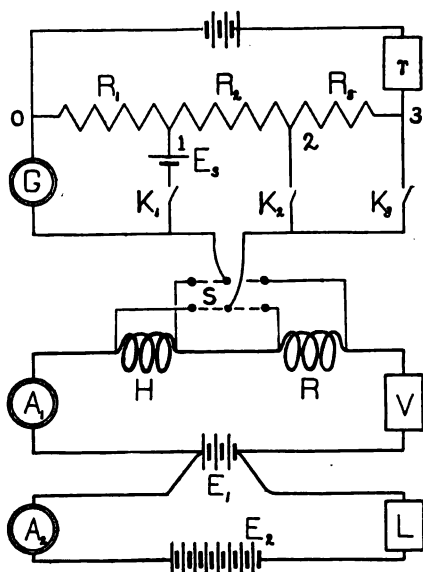


Fig. 2. Showing the electrical setup for measuring the energy supplied to the calorimeter.

them. The closure was effected by using short lengths of soft rubber tubing, the other end being plugged with a short piece of solid glass rod.

ELECTRIC CURRENT FOR HEATING.

Arrangement and Measurement. — Fig. 2 shows the arrangement for measuring the energy supplied to the calorimeter by the electric current. The three storage cells, E_1 , furnished the heating current, which was approximately measured by the ammeter, A_1 . From A_1 the current passed through the heating coil, a standard manganin resistance, and an adjustable resistance, all in series. In order to keep the E.M.F. of E_1 as nearly constant as possible it was joined to eight cells, E_2 , of the laboratory storage battery and sufficient resistance introduced at L to make the current at A_2 very nearly equal to that at A_1 . Thus the battery, E_1 , is continually charged with practically the same current it is supplying, and consequently its E.M.F. is extremely constant. This arrangement might be looked upon as having the main battery at E_2 , while E_1 is an idle battery, "floating across the line" and serving to equalize all the irregularities of the current. Whichever view is taken, the resultant current is much more constant than could be obtained from the use of either battery alone.

The value of this current is determined by measuring the fall of potential over the standard resistance, R . The upper portion of the diagram represents a potentiometer arrangement. R_1 , R_2 , R_3 are certain resistances in a high grade decade Post Office box made by Nalder Bros. R_2 includes all the resistance from 0 to 2, and R_3 is all from 0 to 3. r is a decade 10,000-ohm box which can be varied as required to keep the potentiometer current, i , constant and at such a value that the fall of potential, $R_1 i$, over R_1 equals the E.M.F. of the standard cell, E_s . That is,

$$E_s = R_1 i. \quad (1)$$

This equality is assured when the closing of K_1 produces no deflection of the galvanometer, G . When the double throw switch, S , is thrown to the right, the fall of potential, RI , over the standard resistance, R , is introduced into the galvanometer circuit. If upon closing the key, K_2 , there is no deflection of the galvanometer it means that RI is just balanced by the fall of potential $R_2 i$ of the potentiometer circuit. Or

$$RI = R_2 i. \quad (2)$$

Substituting the value of i from (1) above,

$$I = \frac{E R_2}{R R_1}. \quad (3)$$

The observer having charge of these measurements keeps close watch on this deflection by closing K_2 every few moments and the heating current, I , is maintained at just the value which gives this balance. This adjustment is readily made by means of a copper sulfate liquid resistance in parallel with a portion of the variable resistance. The minimum deflection read corresponded to a change of 1 part in 15,000 in the current. Greater changes than this were noted and the current adjusted to the proper value. When S is thrown to the left the fall of potential, E , over the heating coil is introduced into the galvanometer circuit. R_3 is then adjusted to the value which will give no deflection when K_3 is closed. That is,

$$E = R_3 i = E \frac{R_3}{R_1} \quad (4)$$

For every change made in R_3 there is, of course, a corresponding change made in r in order to keep the potentiometer current, i , constant. When once R_1 , R_2 and R_3 have been adjusted to the proper values no further change is necessary as long as the resistance of the heating coil does not change. The entire work in this part of the experiment is to keep the heating current constant. Once in five minutes the keys K_1 , K_2 , K_3 , are each closed and the corresponding galvanometer readings recorded. If these are not always strictly zero they will be sometimes positive and sometimes negative giving an average of nearly zero for each interval of an hour or two.

The Standard Resistance. — This was a coil of heavy manganin wire wound on a large brass tube after the fashion of the Reichsanstalt standards, the whole being suspended in a permanent bath of paraffin oil. Its resistance was determined by the Carey Foster bridge, and is expressed in terms of the mean of two standard 10-ohm coils made by Otto Wolff and bearing the seal of the Reichsanstalt. As the coil was about 4.63 ohms this comparison could not be made directly, but was obtained by placing the two standard

coils in parallel on the bridge, thus forming a resistance of five ohms with which the manganin coil could be compared directly. The mean of several determinations gave 4.6315 ohms for this resistance at 15° C. and it remained the same as the temperature was raised to 25° C.

The Standard Cell. — The standard cell used in these determinations was a cadmium cell of the *H* pattern and half filled with crystals of cadmium sulfate. Its E.M.F. was 1.01888 international volts at 20° C., that is when expressed in terms of 1.43400 volts for the Clark cell at 15° C. The cell was kept in a bath of kerosene oil and at about 20° C. For slightly different temperatures the value used for its E.M.F. is

$$E_t = 1.01888 - 0.00004(t - 20).$$

For this comparison I am indebted to Dr. W. D. Henderson who was working with the potentiometer at the time and using Professor Carhart's cell No. B₇. This cell has maintained a constant E.M.F. for several years, during which time it has been frequently compared with Clark cells which were carefully set up according to the regular specifications. Its E.M.F. in terms of these Clark cells is therefore very well known, and all comparisons made with it are in reality referred to the Clark cells as the ultimate standard.

Measurement of Time. — The beginning and close of each experiment was on the even minute as read from the second hand of an Elgin watch. No attempt was made to regulate this watch to keep exact time, but shortly after each observation it was compared with the standard clock which was gaining less than a second a day. Thus all of the recorded intervals of time are referred to this standard clock. In a former paper¹ it is shown that the uncertainty in time thus measured is about a tenth of a second; but if it were larger the error thus introduced would be insignificant as one experiment begins when the preceding one ends, and if the recorded duration of one is too long that for the following one will be too short by the same amount. Thus when the average is taken such errors disappear. At the beginning and ending of the day's work there is no such check, but an error of one whole second in eight hours would be insignificant.

¹ PHYS. REV., Vol. XVII., p. 214, Oct., 1903.

CORRECTIONS.

Heat Capacity. — During each experiment the temperature was maintained as nearly constant as possible. There were, however, occasional variations sometimes as great as two or even three hundredths of a degree, but no experiment was brought to a close if the temperature differed from that at the start by as much as one hundredth of a degree. Inasmuch as these slight variations were as often one way as the other, and as no heat was permanently stored in the apparatus through raising its temperature, there is no correction under this head.

Radiation. — As explained above, the outside bath was automatically maintained at a constant temperature, variations of one hundredth of a degree being rare. The calorimeter within the inner chamber will come to a constant temperature, and after standing for one or two days it is safe to assume that it will remain in thermal equilibrium with its surroundings during the short period of an experiment. This being the case, there is no gain or loss of heat by radiation and no correction under this head.

Conduction, Convection, Etc. — All the space about the calorimeter is filled with cotton wool which reduces any circulation of air to a minimum. The only metallic connections with the outside are the four small leading-in wires and the heat conducted in by them is inappreciable.

Starting and Stopping. — In all of the experiments here reported there is practically no starting and no stopping. When the calorimeter is holding a constant temperature with the air current bringing away its steady stream of water vapor and the electric current supplying the equivalent amount of heat, an experiment, so-called, can be made at any time that is convenient. An experiment is really only a single determination of the *time rate* of this stream of vapor, and several such determinations can be made in one day. For this purpose the two H_2SO_4 tubes are inserted in the outcoming air current for a measured interval of time. When these tubes are removed fresh ones are put in their place, and no vapor escapes unmeasured. Such a series of successive determinations are more valuable than the same number of experiments made at different times, because whatever thermal uncertainties may be left at the end

of one run are carried forward to the next. For example, if some part of the calorimeter should be warmer at the close of an experiment than it was at the beginning thereby holding heat which should have been used for the evaporation of water, and during the next run when equilibrium is attained the extra evaporation makes the collected water too large, then the average of these two results will not only possess the usual weight of a mean but it will be an absolute correction of this particular kind of uncertainty. It is for this reason that the experiments are made consecutive, one beginning where the other left off, and a set of four separate determinations made each time.

Stirring. — The water within the calorimeter was vigorously stirred by the passage of the air through it. Ordinarily this stirring would warm the water and necessitate a correction. In this case, however, the bubbles of air are cooled by expansion as they rise through the water. This warming of the water and cooling of the air balance each other and produces no resultant change in temperature.

That this balance is strictly exact in this calorimeter is shown by the following test. The calorimeter was filled to the usual depth with concentrated sulfuric acid, and allowed to assume thermal equilibrium with its surroundings and the water bath by standing for twenty-four hours. The usual air current was then drawn through the calorimeter for four hours. Temperature readings taken every ten minutes varied by a few thousandths of a degree, the maximum range being less than two hundredths. As closely as could be read, the final temperature was the same as the initial reading. It was interesting to watch the conflict between the cooling and warming, for while the thermometer always read about the same the mercury never was still, but was rapidly rising and falling through a range of three or four thousandths, apparently as the bubbles of expanding air played around the bulb of the thermometer or allowed the water to come in contact with it.

The Air Current. — If the air entering the calorimeter does not have the same temperature as the water within, the thermal balance will be destroyed as soon as the air current is started. Before entering the calorimeter the air passes through a long block tin

tube in the bath which warms it to the proper temperature. That no heat or cold is thus carried into the calorimeter by the air current is abundantly shown by the test experiment described above and in which no change in temperature could be detected during the four hours that the air was passing through the calorimeter.

Use of the Thermometer. — During an experiment all the temperature readings were taken on a Beckman thermometer, set so that the mercury stood near the top of the scale where it could be seen and read as only about one degree of the scale projected above the water bath. This thermometer served as an indicator only, and by its aid the temperature of the water in the calorimeter was maintained constant. The actual value of this temperature was determined by a direct comparison of this thermometer at the point where it was used with a standard thermometer, B.S. No. 2,107, which had been recently calibrated by the Bureau of Standards. The corrections then found are used in reducing its readings to the actual temperature.

THE EXPERIMENTS.

Preparation. — As already noted, four consecutive experiments were made at one time. In preparation for each set the calorimeter was filled with fresh distilled water and placed in readiness within the constant temperature chamber. If its temperature differed more than a few tenths of a degree from that of the chamber it was brought nearly up by the electric current. In this condition it was left until the next morning, by which time it reached a stable equilibrium with its surroundings. The proof of this equilibrium is not that the thermometer in the calorimeter reads the same as that in the bath, for this might be so and the calorimeter continue to lose heat to its surroundings. But if the temperature of the calorimeter remains constant for several hours it is safe to assume that it will not gain or lose any heat while remaining under the same external conditions for a few hours longer.

Before recording any measurements there is a preliminary run of about an hour. During this period the dry air is drawn through the calorimeter and the electric current adjusted to a convenient value and one that can be maintained constant. The resistances, R_1 , R_2 , R_3 are adjusted to give zero deflection when their respective

keys are closed. It is seldom that any readjustment is necessary, and it only remains to keep the current at the value which will maintain these balances.

The vapor-laden air leaving the calorimeter must pass through 25 centimeters of tin tubing before reaching the first H_2SO_4 tube. If its temperature is lowered the slightest, water will be deposited on the sides of the tube and thus fail to be collected and weighed. The greater part of this tube is in the water bath, but the last quarter of its length projects into the colder room. This is covered lightly with a thick cloth, under which is an incandescent lamp. This is a necessary precaution and it effectively prevents any deposition of water within the tube. At least two experiments were lost by neglecting this detail.

The Observers. — Two assistants were required whenever a set of experiments were made, and I am indebted to my students in Electrical Measurements, who not only have become deeply interested in this work, but have rendered invaluable service in its accomplishment. One man sits at the galvanometer and maintains the heating current at a constant value. This is monotonous work and he is relieved in two hours by another observer. The other assistant controls the air current, letting just enough through the calorimeter to hold the thermometer reading constant. The time of the writer was fully occupied with the collection of the water vapor, measurements of time, temperature, etc., and seeing that everything went smoothly and well. Every observation and adjustment, except those of keeping constant the air current and the electric current, fell to his lot.

Changing the Tubes. — At the close of the preliminary run and with the calorimeter at precisely its equilibrium temperature, the weighed H_2SO_4 tubes were inserted in the air current. On the even minute, as closely as could be read on the watch, the rubber tube leading to the aspirator was slipped off. The air current through the calorimeter stops entirely, and even circulation of the air is prevented by the deep water trap. There can be no question that the preliminary run is ended and that it ended when the rubber tube was disconnected, although the electric current is still flowing as before. The temporary acid tubes are quickly replaced by the two

that have just been weighed and the rubber tube connected to them, the air being cautiously started through the new tubes in order that a too sudden impact of the air current may not blow out any of the acid. The whole process is completed in a few seconds and all runs on quietly again. The temperature of the calorimeter rises quickly with the stopping of evaporation, but increases only a few hundredths of a degree before it is checked by the starting of the air current. For a few minutes the air current is increased above normal, the increased evaporation quickly reducing the temperature to normal, and then a little below for a few moments.

Thus the water vapor brought away is that evaporated by the heat of the current while the tubes were being changed as well as later, and the experiment begins, strictly, at the ending of the preceding run. Nor can there be an appreciable loss of vapor during the changing of the tubes for the volume that could diffuse out of the end of a five millimeter tube in a few seconds is insignificant when compared with the 160 liters drawn through during the remainder of the run.

Weighing the Tubes.—The tubes were never touched with the fingers but were always handled with a clean cloth. They were weighed on a sensitive balance which was provided with doors at each end of the case. The glass front was always kept closed, even the small weights being introduced through the end door. Thus there was small chance of vapor from the breath condensing on the outside of the tubes or on any part of the balance. During the few moments the tubes were on the balance the rubber caps which closed them from the outside air were removed. Very little water can get into the tube in this short time, while the rubber caps make unsatisfactory and variable weights if left on the tubes. Here again the use of the counterpoise appears. If any water should get into the tube while it is being weighed the counterpoise, being in every way like the other tube, will also gain a like amount. Thus the difference in weight between the two tubes would be unaffected.

RESULTS.

In the following tables are recorded the data obtained in twenty-two experiments, which are all that are entirely free from known

defects or accidents. The preliminary experiments are valueless as the current supply was too unsteady to give them any weight and the weighings were made without the use of a counterpoise. A complete set of experiments at 10° C. was rendered useless by an accident which destroyed the thermal balance of the calorimeter. Some other experiments are discarded because of a leak in the calorimeter by which air, and therefore vapor, from the room could enter and unduly increase the amount of water collected in the H_2SO_4 tubes.

The first table gives the observed time of beginning and ending each experiment. The duration, corrected for the rate of the watch, is expressed in mean solar seconds as measured by the standard clock. The mean reading of the thermometer in the calorimeter is

TABLE I.

Showing the Temperature at which the Water was Evaporated; also the Duration of Each Experiment.

Date.	Duration of Experiments.			Corrected Duration.	Temp. of Water in Calorimeter.	
	Beginning.	End.	Duration.		Therm.	Temp.
1907.			secs.	T.	(ave.)	
Feb. 7	11 : 00 : 00	1 : 00 : 00	7,200	7,197	4.982	21.18
"	1 : 00 : 00	3 : 00 : 00	7,200	7,197	4.988	21.19
"	3 : 00 : 00	5 : 00 : 00	7,200	7,197	4.975	21.18
Feb. 8	9 : 00 : 00	11 : 00 : 00	7,200	7,197	4.961	21.16
"	11 : 00 : 00	1 : 00 : 00	7,200	7,197	4.963	21.16
"	1 : 00 : 00	3 : 00 : 00	7,200	7,197	4.961	21.16
"	3 : 00 : 00	5 : 00 : 00	7,200	7,197	4.965	21.16
Feb. 9	11 : 00 : 00	1 : 00 : 00	7,200	7,197	5.004	21.20
"	1 : 00 : 00	3 : 00 : 00	7,200	7,196	4.997	21.20
"	3 : 00 : 00	5 : 00 : 00	7,200	7,197	5.000	21.20
Mar. 9	9 : 40 : 00	11 : 40 : 00	7,200	7,197	5.865	21.14
"	11 : 40 : 00	1 : 05 : 00	5,100	5,098	5.869	21.15
Mar. 16	9 : 20 : 00	11 : 20 : 00	7,200	7,203	4.796	13.96
"	11 : 20 : 00	1 : 40 : 00	8,400	8,404	4.788	13.95
"	1 : 40 : 00	3 : 35 : 00	6,900	6,903	4.788	13.95
"	3 : 35 : 00	5 : 40 : 00	7,500	7,504	4.790	13.95
Mar. 23	10 : 10 : 00	12 : 10 : 00	7,200	7,205	4.577	28.06
"	12 : 10 : 00	2 : 11 : 00	7,260	7,265	4.579	28.06
"	2 : 11 : 00	3 : 40 : 00	5,340	5,344	4.577	28.06
"	3 : 40 : 00	5 : 10 : 00	5,400	5,403	4.574	28.06
Apr. 6	9 : 45 : 00	11 : 45 : 00	7,200	7,202	4.324	39.80
"	11 : 45 : 00	1 : 45 : 00	7,200	7,203	4.325	39.80

TABLE II.

Giving the Amount of Water Evaporated within the Calorimeter During Each Experiment.

Date.	Tube.	Weighings.			Water Evaporated.
		Before.	After.	Gain.	
Feb. 7	E	26.1696	29.2330	3.0634	3.0634
	G	29.1052	29.1050	0000	
"	B	25.8130	28.8696	3.0566	3.0566
	C	21.5766	21.5765	0000	
"	E	29.2330	32.3020	3.0690	3.0704
	G	29.1050	29.1064	0014	
Feb. 8	B	28.8722	31.9287	3.0565	3.0565
	C	21.5769	21.5765	0000	
"	E	32.3043	35.3730	3.0687	3.0722
	G	29.1065	29.1080	0035	
"	B	31.9287	34.9888	3.0601	3.0618
	C	21.5765	21.5782	0017	
"	E	35.3730	38.4238	3.0508	3.0573
	G	29.1090	29.1155	0065	
Feb. 9	E	38.4246	41.4660	3.0414	3.0571
	G	29.1130	29.1287	0157	
"	B	38.0310	41.0634	3.0324	3.0619
	C	21.5836	21.6131	0295	
"	E	41.4660	44.5012	3.0352	3.0573
	G	29.1287	29.1508	0221	
Mar. 9	B	29.8615	32.6373	2.7758	2.7809
	C	21.6228	21.6279	0051	
"	E	34.0210	35.9190	1.8980	1.9014
	G	29.1545	29.1579	0034	
Mar. 16	B	36.0128	37.8443	1.8315	1.8567
	C	21.6298	21.6550	0252	
"	E	37.2865	39.4596	2.1731	2.1740
	G	29.1583	29.1592	0009	
"	B	37.8443	39.6200	1.7757	1.7872
	C	21.6550	21.6665	0115	
"	E	39.4596	41.4018	1.9422	1.9424
	G	29.1592	29.1594	0002	
Mar. 23	E	33.5136	36.6135	3.0999	3.1007
	G	39.5398	39.5406	0008	
"	B	27.9066	31.0345	3.1279	3.1298
	C	25.0065	25.0084	0019	

TABLE II.—*Continued.*

Giving the Amount of Water Evaporated within the Calorimeter During Each Experiment.

Date.	Tube.	Weighings.			Water Evaporated.
		Before.	After.	Gain.	
Mar. 23	E	36.6135	38.9152	2.3017	2.3017
	G	39.5406	39.5404	0000	
"	B	31.0345	33.3560	2.3215	2.3249
	C	25.0084	25.0118	0034	
Apr. 6	B	33.3567	36.5984	3.2417	3.2461
	C	25.0072	25.0116	0044	
"	E	38.9135	42.1544	3.2409	3.2528
	G	39.5372	39.5491	0119	

shown in next to the last column. The scale was divided into hundredths of a degree and easily read to thousandths. It was thus comparatively easy to keep the temperature variations within one or two hundredths of a degree. The actual temperature is given in the last column, these values being in terms of thermometer "B.S. 2107" as corrected by the certificate of the Bureau of Standards dated Dec., 1906.

Table II. gives the weighings of the H_2SO_4 tubes. As there were always two of these in series the gain in weight of both is taken as giving the total amount of water collected by them. It will be noticed that the second tube gains an appreciable amount only after the first one has caught several grams of water.

The electrical measurements are recorded in Table III. During the experiments at about $21^\circ C.$ the standard cell, in its beaker of kerosene, was kept in one corner of the constant temperature bath. When the bath was changed to other temperatures the cell was placed in a large tank of water in an adjoining room where its temperature would change but slowly, and always be moderate.

The resistances, R_1 , R_2 , R_3 , have the significance shown in Fig. 2. The 218.9 ohms under R_2 is applied as a correction because of a voltmeter current through the standard during the first three days in addition to the heating current. It required 218.9 ohms in R_2 to balance this voltmeter current alone: hence this is to be subtracted from the total of 4,000 ohms to give the resistance necessary to

TABLE III.

The Electrical Measurements, Showing the Energy Supplied by the Electric Current for the Evaporation of Water.

Date.	Standard Cell.		Box Coils—as Marked.			Calibration Corrections.			Gal. Readings.			Corrections.			Corrected Resistances.			R	R_2 $E=E_2 R_1$	E, R_2 $I=RR_1$
	Temp.	E_s	R_1	R_2	R_3	r_1 ohms.	r_2 ohms.	r_3 ohms.	d_1 mm.	d_2 mm.	d_3 mm.	r_1' ohms	r_2' ohms	r_3' ohms	R_1	R_2	R_3			
Feb. 7	21.1	1.01893	3,000	4,000	11,077	+32	+02	+55	0	0	+7	0	0	-3.3	3,000.3	3,781.1	11,074.2		3.7609	.27725
"	"	"	"	-218.9	"	"	"	"	0	-3	+1	+1.4	0	-5	"	3,782.5	11,077.0		3.7618	.27735
"	"	"	"	"	"	"	"	"	0	-6	-1	+3.0	+5	"	"	3,784.1	11,078.0		3.7621	.27747
Feb. 8	"	"	"	"	11,074	"	"	"	0	0	0	0	0	0	"	3,781.1	11,074.5		3.7610	.27725
"	"	"	"	"	"	"	"	"	0	+1	-4	-5	+2.0	"	"	3,780.6	11,076.5		3.7617	.27721
"	"	"	"	"	"	"	"	"	0	-1	-2	+5	+1.0	"	"	3,781.6	11,075.5		3.7613	.27729
"	"	"	"	"	11,074.7	"	"	"	0	+1	-1	-5	+5	"	"	3,780.6	11,075.7		3.7614	.27721
Feb. 9	"	"	"	"	11,075	"	"	"	0	0	-3	0	+1.2	"	"	3,781.1	11,076.7		3.7617	.27725
"	"	"	"	"	"	"	"	"	0	0	0	0	0	"	"	3,781.1	11,075.5		3.7613	.27725
"	"	"	"	"	"	"	"	"	0	+1	0	-5	0	"	"	3,780.6	11,075.5		3.7613	.27721
Mar. 9	"	"	"	6,000	6,337.9	"	+22	+33	0	0	+1.7	0	-3.2	"	"	6,000.2	6,335.0		2.1514	.43997
"	"	"	"	"	6,113.6	"	"	+25	0	-1	+4.1	+2	-7.7	"	"	6,000.3	6,106.2		2.0737	.43998
Mar. 16	19.2	1.01885	"	3,000	8,539.5	"	+32	+76	0	0	+1	0	-2	"	"	3,000.3	8,540.1		2.9000	.21998
"	20.0	1.01888	"	"	8,539	"	"	"	0	0	+3	0	-5	"	"	3,000.3	8,539.3		2.9000	.21999
"	20.8	1.01891	"	"	"	"	"	"	0	0	0	0	0	"	"	3,000.3	8,539.8		2.9001	.22000
"	21.6	1.01894	"	"	8,538.6	"	"	"	0	-1	-1	+2	+2	"	"	3,000.5	8,539.6		2.9001	.22002
Mar. 23	25.0	1.01907	4,000	5,000	14,961	+02	-08	+94	0	0	0	0	0	0	4,000.0	4,999.9	14,961.9	The resistance was 4.6315 ohms in each experiment.	3.8118	.27503
"	25.0	1.01907	"	"	"	"	"	"	0	0	+1	0	-5	"	"	"	14,961.4		3.8117	.27503
"	25.2	1.01908	"	"	"	"	"	"	0	0	0	0	0	"	"	"	14,961.9		3.8119	.27504
"	25.7	1.01910	"	"	"	"	"	"	0	0	+1	0	-5	"	"	"	14,961.4		3.8118	.27504
Apr. 6	20.4	1.01890	"	"	15,494	"	"	+79	0	0	0	0	0	"	"	"	15,494.8		3.9468	.27499
"	21.8	1.01895	"	"	"	"	"	"	0	0	0	0	0	"	"	"	15,494.8		3.9470	.27500

balance the heating current alone. In some cases the value of R_s was changed during an experiment. The recorded value is then the time average of the different actual resistances which explains the decimal numbers in this column. The resistance coils of this box were carefully compared with each other by the Carey Foster method and the corrections thus found are shown in the columns, r_1, r_2, r_3 ; r_1 being the correction to be added to R_1 , and similarly for the others. As the ratio of two of these resistances is always used the temperature correction does not enter.

The galvanometer readings, d_1, d_2, d_3 , are the time averages of the readings observed on closing the keys, K_1, K_2, K_3 , respectively. These readings are always small and as some are positive and others negative the resultant sum for a two hour period is nearly zero. If it is not zero it means that the current was not kept at quite the assigned value. The columns r'_2 and r'_3 show the amounts by which R_2 and R_3 should have been changed to exactly balance the actual current which went to the heating coil. Both sets of corrections are applied to give the "corrected resistances." The temperature of the standard resistance, R_s , was read and recorded for each experiment. The lowest was 15°C. on March 16, and the highest was 25°C. on April 6. Its resistance was 4.6315 ohms. with no change in these five figures for this range of temperature,

The last column gives the current, I , through the heating coil within the calorimeter, the values being computed by the formula at the top of the column. The fall of potential, E , over the same coil is given in the preceding column. The values of E are expressed in terms of 1.43400 volts for the E.M.F. of a Clark cell at 15°C. The unit of current here used is such that 1.43400 amperes flowing through one international ohm will produce a potential difference equal to the E.M.F. of a Clark cell at 15°C.

The final results are collected in Table IV. which is largely self-explanatory. The last column gives the heat of evaporation computed by the formula at the top of the column. These values are in sets corresponding to the four different temperatures at which they were determined. The large number of determinations at 21°C. were made partly because the value of L at this temperature was most desired, but largely to test the reliability and accuracy of the

method. Each day's work stands independently, the apparatus being dismantled and the calorimeter refilled with a fresh supply of distilled water for each set of determinations.

Although only two values were obtained on March, yet these are especially valuable as the calorimeter used on that date was one of the earliest forms. These determinations are therefore free from any constant bias due to the particular form of calorimeter used and which might affect all the others. It will be noticed, however, that these two results agree very closely with the others obtained at the same temperature.

TABLE IV.

Collected Data. Giving the Results Obtained in Each Experiment.

Date.	Temperature of Water.	Water Evaporated.	Duration.	E	I	$L = \frac{EIT}{W}$
		grams.	secs.	volts.	amperes.	joules.
Feb. 7	21.18	3.0634	7,197	3.7609	.27725	2,449.7
"	21.19	3.0566	7,197	3.7618	.27735	2,456.6
"	21.18	3.0704	7,197	3.7621	.27747	2,446.8
Feb. 8	21.16	3.0565	7,197	3.7610	.27725	2,455.3
"	21.16	3.0722	7,197	3.7617	.27721	2,442.8
"	21.16	3.0618	7,197	3.7613	.27729	2,451.6
"	21.16	3.0573	7,197	3.7614	.27721	2,454.5
Feb. 9	21.20	3.0571	7,197	3.7617	.27725	2,455.2
"	21.20	3.0619	7,197	3.7613	.27725	2,451.2
"	21.20	3.0573	7,197	3.7613	.27721	2,454.5
Mar. 9	21.14	2.7809	7,197	2.1514	.43997	2,449.7
"	21.15	1.9014	5,098	2.0737	.43998	2,446.3
Mar. 16	13.96	1.8567	7,203	2.9000	.21998	2,474.9
"	13.95	2.1740	8,404	2.9000	.21999	2,466.2
"	13.95	1.7872	6,903	2.9001	.22000	2,464.3
"	13.95	1.9424	7,504	2.9001	.22002	2,465.1
Mar. 23	28.06	3.1007	7,205	3.8118	.27503	2,436.0
"	28.06	3.1298	7,265	3.8117	.27503	2,433.4
"	28.06	2.3017	5,344	3.8119	.27504	2,434.1
"	28.06	2.3249	5,403	3.8118	.27504	2,436.4
Apr. 6	39.80	3.2461	7,202	3.9468	.27499	2,408.0
"	39.80	3.2528	7,203	3.9470	.27500	2,403.6

The mean value of L for each temperature is,

Temperature.	Heat of Evaporation.
13.95	2,467.6
21.17	2,451.2
28.06	2,435.0
39.80	2,405.8

These values are plotted as ordinates of the lower curve in Fig. 3, which is the straight line that most nearly represents the points. A slightly convex curve would fit the observations better and might possibly be nearer the truth. But in view of the uncertainty regarding the location of such a curve at 100° C. it is deemed best to merely draw the nearest straight line, as this represents the results

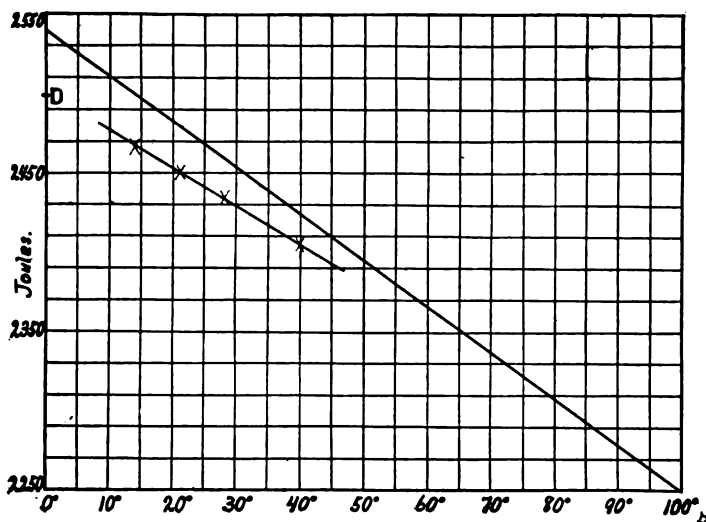


Fig. 3. The short curve gives the values of L for 10° C. to 40° C. For comparison Regnault's formula is plotted from 0° C. to 100° C. Dieterici's value is shown at D .

sufficiently well over the range of temperature which has been investigated.

The individual determinations are too close to each other to appear as separate points and only the mean value for each temperature is shown. In computing the probable error of the curve however, each one of the twenty-two experiments is given an equal weight, the line being drawn to make this a minimum. The equation of this line is

$$L = 2,502.5 - 2.43T$$

where T is the temperature Centigrade and L is given in international joules.

OTHER INVESTIGATIONS.

Dieterici. — Undoubtedly the best determination previously made of the heat of evaporation of water at low temperatures is that of

Dieterici. In 1889 he evaporated water within a Bunsen ice calorimeter. The water was placed in a small bulb within the inner tube of the calorimeter. When thermal equilibrium was attained the water was all evaporated by reduced pressure, the heat required being furnished by the further freezing of the ice mantle. Assuming that one mean calorie expelled 0.01544 gram of mercury, he obtained¹ the value 596.80 mean calories for the heat of evaporation at 0° C.

Using the best modern apparatus and methods he has recently determined² that 0.015491 gram of mercury corresponds to one mean calorie. In a later investigation with the Bunsen calorimeter and in which the heat was generated by an electric current, Dieterici finds³ that it requires 4.1925 joules to draw 0.015491 gram of mercury into the calorimeter. The electrical units are expressed in terms of a Weston element, and probably the result is given in Reichsanstalt joules. Since Reichsanstalt volts are larger than international volts by the factor 1.00081, and this factor enters twice in the expression for joules, we have for the heat of evaporation of water at 0° C.,

$$\begin{aligned} L &= 596.80 \times \frac{.015440}{.015491} \times 4.1925 \times (1.00081)^2 \\ &= 2497.9 \text{ international joules,} \end{aligned}$$

that is, when expressed in terms of 1.43400 volts for a Clark cell at 15° C. This value is shown at the point *D*, Fig. 3.

Regnault. — Regnault's familiar equation, $L = 606.5 - 0.695T$, extrapolated largely from results between 63° C. and 230°⁴ C. is known to give much too large values at low temperatures, and even Regnault recognized that his determinations at low temperatures were not as reliable as those at the higher temperatures. Yet, strange as it may seem, these values are quoted to-day more often than the results of all other determinations combined. Partly for this reason, the above equation is plotted in Fig. 3, and it shows clearly how much larger values it gives than those which have since

¹ Ann. der Phys., Vol. 37, p. 504, 1889.

² Ann. der Phys., Vol. 16, p. 603, 1905.

³ Ann. der Phys., Vol. 16, p. 619, 1905.

⁴ Institute de France, Mem. Acad. Sci., Vol. 21, pp. 1-748, 1847.

been determined. The individual determinations vary considerably among themselves and cannot be accorded much weight.

Some years later Regnault made two series of experiments¹ in which dry air was drawn through the water. The results were not very satisfactory. The mean of the first series agreed quite closely with his formula, but the second series gave results two per cent. above the formula. Regnault accepted the result with the remark that this discrepancy should be looked into, but he recorded no further experiments along this line. In fact his apparatus was ill-fitted for such work, as the corrections amounted to a large fraction of the total measurements. He accepted these results, however, as demonstrating that the heat required to slowly evaporate water into air at atmospheric pressure is the same as when it boils rapidly under reduced pressure.

Griffiths. — Some years ago Griffiths made an elaborate investigation² into the heat of evaporation of water. His original intention was to cover the range from 10° C. to 60° C., but only a few results at 30° C. and at 40° C. are given, and he says "had time permitted I should have performed more experiments especially at 30° C." His preliminary method was to draw dry air through the water, but this failed to give concordant results and the final determinations were made by the more common method of reduced pressure.

A weighed amount of water was placed in a glass tube within the calorimeter and flowed out through a fine opening as fast as it was evaporated. Heat was supplied by an electric current which was stopped, as nearly as possible, when the last of the water was evaporated. The experiments were conducted at a constant temperature and appear to have been very carefully performed. The heat furnished by the current was computed from the formula $H = E^2 T / R$, the value of E being measured in terms of a Clark cell the E.M.F. of which was taken as 1.4342 volts at 15° C. He expressed his results in calories, using 4.199 for the mechanical equivalent of heat. Using the same factor to translate the results back into joules gives

2429.3 joules at 30°.00 C.
and 2403.6 joules at 40°.15 C.

¹ *Institute de France, Mem. Acad. Sci.*, Vol. 26, pp. 883-906, 1862.

² *Phil. Trans.*, Vol. 186 A, pp. 261-342, 1895.

when expressed in terms of 1.43400 volts for the Clark cell at 15° C.

Probably these determinations at 30° C. and at 40° C. are reliable; but it is questionable whether his formula, $L = 596.73 - .601 T$, should be extrapolated to 0° C. and 100° C. To be sure it thus agrees at 100° C. with Regnault's published value, but there is reason to believe that this is too low. At 0° C. the formula, as expressed in calories, is identical with Dieterici's results as first published. As now corrected the latter values are lower by 1 part in 300, thus leaving the formula without experimental basis below 25° C.

Henning. — During the progress of this work there has appeared¹ the account of a similar investigation for the range from 50° C. to 100° C. A few determinations were made at 30° C. but for some reason are given only one eighth the weighting accorded the determinations at each of the higher temperatures. The water was made to boil under reduced pressure, the vapor being condensed and weighed. Heat was supplied by an electric current and measured in terms of a Weston standard cell. Probably the results were obtained in terms of Reichsanstalt volts. They are expressed in 15-degree calories by means of the factor 4.188 joules per calorie. I have reduced them back to international joules by multiplying by this same factor and also by 1.0016.

Results of Other Investigations.

	Temperature.	Heat of Evaporation.	
		As Reported.	As Computed.
Dieterici.	0	Calories. 596.80	International Joules 2,497.9
Griffiths.	30.00	578.70	2,429.3
"	40.15	572.60	2,403.6
Henning.	30.12	579.0	2,428.7
	49.14	569.55	2,389.0
	64.85	559.47	2,346.8
	77.34	552.47	2,317.4
	89.29	545.76	2,289.3
	100.59	538.25	2,257.8

Whether expressed in calories or joules, most of the results appear rather high. This is very apparent at 100° C. where the

¹ Ann. der Phys., Vol., 21, pp. 849-878, 1906.

familiar number 537 is exceeded by nearly two units. However Henning is not alone in finding this larger value, and it may be that the accepted value is too low. Certain it is that this important constant should be redetermined with modern appliances and with a greater degree of precision than has yet been done.

In the preceeding table are collected the results mentioned above :

SUMMARY.

1. Water is evaporated by passing through it a stream of dry air. As now developed, this method has proved entirely satisfactory and can be used for any temperature at which the surrounding water bath can be maintained constant. The usual method of boiling water under reduced pressure is not suitable for low temperatures as it is difficult to maintain constant and steady evaporation. This explains why previous investigators have confined their work to the higher temperatures. With the present method the temperature of the evaporating water remains constant, and all thermal corrections are eliminated.

2. The heat of evaporation of water at temperatures between 14°C. and 40°C. is given by the formula

$$L(\text{in joules}) = 2502.5 - 2.43T.$$

The "probable error" of values computed from this formula is 0.5 joule.

3. These results are expressed in international joules : that is, in terms of the international ohm and 1.43400 volts for the E.M.F. of the Clark cell at 15°C. They are thus given in terms of a definite and reproducible unit. Should the E.M.F. of the Clark cell be found to be less than this value by 1 part in 1,000, all of the results here reported will be decreased by 2 parts in 1,000. They will then be expressed in terms of the new unit as exactly as they are now given in international joules.

4. It is interesting to note that the results obtained by this method are in line with those of Dieterici at 0°C. and those of Griffiths at higher temperatures, although obtained by totally different methods. It might be inferred, *a priori*, that it would require the same amount of heat to evaporate a gram of water whether the

external pressure be great or small. Nevertheless it is a source of satisfaction to have this experimental demonstration that the heat of evaporation is independent of the pressure.

5. The value of the heat of evaporation at five degree intervals is given in the following table. For comparison the results are also given in mean calories, assuming that a mean calorie is equivalent to 4.1887 international joules.¹

This makes the formula read

$$L \text{ (in mean calories)} = 597.44 - .580 T.$$

Heat of Evaporation of Water.

Temperature Centigrade.	International Joules.	Mean Calories.	Temperature Centigrade.	International Joules.	Mean Calories.
10	2,478.2	591.64	30	2,429.6	580.04
15	2,466.0	588.73	35	2,417.4	577.12
20	2,453.9	585.84	40	2,405.3	574.24
25	2,441.7	582.93	45	2,393.1	571.33

UNIVERSITY OF MICHIGAN,

June 1, 1907.

¹ Phil. Trans., Vol. 199 A, p. 149, 1902.

SPECIFIC HEAT OF SOLUTIONS. V.

BY WILLIAM FRANCIS MAGIE.

1. This paper is a continuation of others, published under the same title in previous volumes of this REVIEW. It deals with the heat capacities of electrolytic solutions and the possibility of representing them by a simple formula involving the dissociation factor. Most of the measurements of heat capacity employed are those of Julius Thomsen.¹ The measurements of solutions of potassium chloride were made by myself, and those of sodium and potassium nitrate, barium and strontium chloride, and barium and strontium nitrate by Mr. R. E. Trone, Instructor in physics at Princeton University. The calorimeter used by us was the modified form of the Pfaundler calorimeter described in No. III. of this series. It gives me pleasure to have an opportunity to express my obligations to Mr. Trone for his faithful and accurate work.

The volumes of electrolytic solutions exhibit in general the same peculiarities as their heat capacities, and admit of representation by a similar formula. I have accordingly introduced a discussion of these volumes *pari passu* with that of the heat capacities. Most of the measurements of volume employed were made by Thomsen.² Those for strontium chloride were worked over from data given by Kohlrausch and Holborn.³ Mr. Trone, using a standardized Mohr's balance, contributed those for barium chloride and for barium and strontium nitrate.

2. *Peculiarity of the Heat Capacities of Electrolytes.* — The solutions which Thomsen studied were made up by dissolving one gram-molecule of the solute in some known number, N , of gram-molecules of water. The heat capacity of such a solution was determined and the heat capacity of the N gram-molecules of water subtracted

¹ Thermodynamische Untersuchungen, Vol. I., Pogg. Ann., 142, p. 335.

² L. c.

³ Leitvermögen der Elektrolyte, p. 145.

from it. The difference gave the apparent heat capacity of one gram-molecule of the solute — or its apparent molecular heat — in a solution of that concentration. It was found that the apparent molecular heat of the solute generally diminishes with increasing dilution, so that in practically all cases it becomes negative long before the solution becomes very dilute.

Similarly, the apparent molecular volumes of the same solutes diminish with increasing dilution, though it is only in a very few cases that they become negative within the range of Thomsen's observations.

3. *General Conclusion.* — These results demonstrate that in solutions, at least in electrolytic solutions, the water is affected by the presence of the solute in such a way that its heat capacity and specific volume are diminished.¹ They are therefore conclusive in favor of some form of what we may call the association theory of solutions, in distinction from that theory of solutions in which the solute is considered as having the properties of a gas, and the solvent as being merely an inert medium in which the molecules or ions of the solute are suspended. As will be seen later, they indicate that the association between the molecules or ions of the solute and the water, within the range of concentration covered by the observations, is fairly definite in its effects, so that we may conceive of each molecule or ion of solute as surrounded by a group of a definite number of water molecules, which are within its sphere of influence and affected by it. There is little or no evidence that the numbers of water molecules in these groups change with the concentration. In this respect the hypothesis which will explain the results under consideration differs from that adopted by Jones and his fellow-workers² to explain the abnormalities of the freezing and boiling points observed by them in concentrated solutions.

The conclusion that the negative values of the apparent molecular heats prove that the heat capacity of the water is affected by the presence of the solute has already been drawn by Tammann.³

¹ Magie, *Bull. Am. Phys. Soc.*, Vol. 2, no. 2; this REVIEW, XIII., p. 91; XVIII., p. 449.

² *Am. Chem. Jour.*, 23, p. 89; *Zeitschrift für Phys. Chem.*, XLVI. p. 244; XLIX., p. 385; this REVIEW, XVIII., p. 146.

³ *Zeitschrift für Phys. Chem.*, XVIII., p. 625.

4. *Formulas to Represent Heat Capacities and Volumes of Solutions.*—An examination of the tables which follow will show that the heat capacities of the solutions of any one solute, made up by dissolving one gram molecule of the solute in N gram-molecules of water, may be represented by the formula

$$H = WN + A + Bp.$$

In this formula W is the molecular heat of water, or 18, A and B are constants, and p is the dissociation factor, obtained in the usual way as the ratio of the molecular conductivity of the solute in a solution of the given concentration to the molecular conductivity of the same solute in an infinitely dilute solution. The values of p are calculated from the molecular conductivities given in the tables of Kohlrausch and Holborn, with the help of their tables of specific gravities.

A similar formula,

$$V = UN + D + Ep,$$

will represent the volumes of the various solutions. In this formula U is the molecular volume of water, D and E are constants, and p again the dissociation factor.

NaCl. $A = 39$, $B = -70$; $D = 25.86$, $E = -12$

N	p	H Obs. Th.	H Calc.	V Obs. Th.	V Calc.
10	0.42			200.9	200.8
20	.544	361	361.0	379.3	379.3
30	.613	536	536.1	558.4	558.5
50	.668	892	892.2	917.8	917.8
100	.729	1,788	1,788.0	1,816.1†	1,817.1
200	.780	3,578†	3,584.4	3,616.0	3,616.4

KCl. $A = 96$, $B = -149$; $D = 47$, $E = -25$.

N	p	H Obs. M.	H Calc.	V Obs. Th.	V Calc.
15	0.672			300.4	300.2
30	.728			569.0	568.8
50	.753	880.7	882.0	928.2	928.2
100	.787	1,777.6	1,777.2	1,827.3	1,827.3
200	.818	3,571.8	3,572.2	3,625.0	3,626.0
300	.835	5,370.2	5,370.2		
400	.848	7,167.1	7,168.1		

¹ The letters *Th.*, *M.*, *Tr.*, *K.* prefixed to the tabulated observations, indicate the various observers, Thomsen, Magie, Trone, Kohlrausch.

NH_4Cl . $A = 39$, $B = -62.1$; $D = 43.5$, $E = -7.5$.

N	ρ	H Obs. T_k	H Calc.	V Obs. T_k	V Calc.
10	0.593	181.6	182	219.0	219.1
25	.703	443.6	445	488.2	488.2
50	.742	893	893	937.8	937.9
100	.777	1,791	1,791	1,837.7	1,837.7
200	.806	3,588	3,589	3,637.6	3,637.5

HCl . $A = 4$, $B = -41$; $D = 27$, $E = -10.56$.

N	ρ	H Obs. T_k	H Calc.	V Obs. T_k	V Calc.
20	0.596	339	339.6	379.2	380.7
50	.773	873	872.4	918.8	918.8
100	.84	1,770	1,769.6	1,818.5	1,818.1
200	.877	3,561†	3,568	3,617.7	3,617.7

$NaOH$. $A = 32$, $B = -65.6$; $D = 7$, $E = -15$.

N	ρ	H Obs. T_k	H Calc.	V Obs. T_k	V Calc.
30	0.602	533	533	537.9	538
50	.696	885	886	896.4	897
100	.775	1,781	1,781	1,795.9	1,795.4
200	.824	3,578	3,578	3,594.8	3,594.7

KOH . $A = 59$, $B = -110$; $D = 22$, $E = -21$.

N	ρ	H Obs. T_k	H Calc.	V Obs. T_k	V Calc.
30	0.69	522	523	547.5	547.6
50	.76	876	875	906.3	906.1
100	.82	1,770	1,769	1,804.9	1,804.8
200	.855	3,565	3,565	3,604.1	3,604.1

$\frac{1}{2}H_2SO_4$. $A = 27.5$, $B = -40$; $D = 22$, $E = -10$.

N	ρ	H Obs. T_k	H Calc.	V Obs. T_k	V Calc.
9.5	0.337	180.6	185	189.8	189.6
24.5	.463	450	450	458.3	458.4
49.5	.510	898.5	898.1	907.7	907.9
99.5	.532	1,797.5	1,797.5	1,807.7	1,807.7

$NaNO_3$. $A = 55$, $B = -75$; $D = 37.5$, $E = -13.5$.

N	ρ	H Obs. T_k	H Calc.	V Obs. T_k	V Calc.
10	0.34			212.5	213
25	.514			480.4	480.7
50	.618	908.2	908.6	929.2	929.2
100	.698	1,802.7	1,802.7	1,828.2	1,828.2
200	.757	3,598	3,598.2	3,627.0	3,627.5
300	.785	5,396	5,396.1		

KNO_3 . $A = 78$, $B = -120$; $D = 47.5$, $E = -12$.

N	ρ	H Obs. Tr.	H Calc.	V Obs. Tr.	V Calc.
25	0.55	458.6	462	490.7	490.9
50	.633	902.2	902.1	939.8	939.8
100	.705	1,793.6	1,793.4	1,839.2	1,839.1
200	.76	3,586.6	3,586.8	3,638.3	3,638.4
300	.79	5,383.8	5,383.2		
400	.81	7,182.0	7,180.8		

$\frac{1}{2}BaCl_2$. $A = 10$, $B = -65$; $D = 29.2$, $E = -25$.

N	ρ	H Obs. Tr.	H Calc.	V Obs. Tr.	V Calc.
50	0.548	875.5	874.4	915.2	915.5
100	.606	1,770.5	1,770.6	1,814.2	1,814.1
200	.662	3,567	3,566.9	3,612.8	3,612.7
300	.69	5,365.6	5,365.2	5,411.8	5,412.0

$\frac{1}{2}SrCl_2$. $A = 16.6$, $B = -76$; $D = 18.8$, $E = -10$.

N	ρ	H Obs. Tr.	H Calc.	V Obs. Tr.	V Calc.
50	0.56	873.5	874	912.6	913.2
100	.62	1,770.3	1,769.6	1,812.6	1,812.6
150	.66	2,666.3	2,666.6	2,712.3	2,712.2
200	.681	3,565.4	3,564.9	3,612.0	3,612.0
300	.717	5,361.5	5,362.1	5,411.6	5,411.6

$\frac{1}{2}Ba(NO_3)_2$. $A = 31$, $B = -76$; $D = 25.3$, $E = 0$.

N	ρ	H Obs. Tr.	H Calc.	V Obs. Tr.	V Calc.
100	0.469	1,795.7	1,795.4	1,825.5	1,825.3
150	.526			2,725.3	2,725.3
200	.563	3,588.4	3,588.2	3,625.3	3,625.3
250	.593			4,525.3	4,525.3
300	.618	5,382.3	5,384.0	5,426.3	5,425.3

$\frac{1}{2}Sr(NO_3)_2$. $A = 9$, $B = -40$; $D = 24.8$, $E = -3$.

N	ρ	H Obs. Tr.	H Calc.	V Obs. Tr.	V Calc.
50	0.442	895	892	923.5	923.5
100	.533	1,787.8	1,788	1,823.2	1,823.2
200	.607	3,584.8	3,584.7	3,623.0	3,623.0
300	.648	5,383.5	5,383.1		

The dissociations used here were determined by Professor William Foster (this REVIEW, VIII., p. 257). The curve of dissociations, plotted from Kohlrausch's data, is suspiciously irregular.

A few of the observations in these tables are marked with a (+). They differ by more than the probable error from the calculated numbers. In every one of these cases, if the curve of specific heats or of specific gravities is plotted, it will be found that the discordant result corresponds to an aberrant part of the curve; and when the curve is smoothed, the heat capacity or the volume calculated from the smoothed curve is in good accord with the quantity calculated from the formula. I think there can be no doubt that these discrepancies are due to experimental errors, and that it is legitimate to remove them by smoothing the curves. An error of two tenths of one per cent. in the determination of the specific heat would account for the largest discrepancy found.

6. *Deduction of Formulas.*—The formulas given in § 4, from which the results of the tables have been calculated, admit of a simple interpretation. Let us suppose that n gram-molecules of the solute are dissolved in N gram-molecules of water, and that p gram-molecules of solute are dissociated into ions. Let us suppose further that each actual molecule and each ion of the solute collects around itself a group of water molecules and in general affects and modifies the heat capacity of the group. The heat capacity of the solution is additive of the heat capacities of the several homogeneous parts of the solution, and on our suppositions is the sum of the heat capacities (1) of the water outside the groups of water molecules affected by the solute; (2) of the undissociated molecules and the water affected by them; (3) of the ions and the water affected by them. This sum may be written out by the help of the following symbols:

M, S, N , molecular weight, specific heat, number of gram-molecules of water.

m, n , molecular weight, number of gram-molecules of solute.

p , number of gram-molecules dissociated into ions.

a, u , number of water molecules affected by one undissociated gram-molecule of solute, and by one dissociated gram-molecule of solute, respectively.

s, σ , specific heats of the groups containing an undissociated molecule of solute and a dissociated molecule of solute, respectively.

The heat capacity of the solution may be written,

$$\begin{aligned} H &= S(MN - a(n-p)M - apM) + s(m+aM)(n-p) + \sigma(m+aM)p \\ &= SMN + (sm + saM - SaM)(n-p) + (\sigma m + \sigma aM - SaM)p \\ &= WN + A(n-p) + Cp, \end{aligned}$$

in which WN is the heat capacity of the water used in making up the solution; A is a constant depending upon the undissociated molecules and the way they affect the water; C is a constant depending in a similar way upon the dissociated molecules, or the ions formed from them, and the way they affect the water.

In case n equals 1, p is the dissociation factor, and the formula then becomes

$$H = UN + A + Bp,$$

in which $B = C - A$.

On the same suppositions as to the constitution of a solution, its volume may be considered as the sum of the volumes of those parts of the solution whose heat capacities have been added to express the heat capacity of the solution. Writing out in a similar way the sum of these volumes, we find that the volume of the solution is expressed by a formula of the same form as that obtained to express the heat capacity. In this formula, which may be written in the form

$$V = UN + D + Ep,$$

UN is the volume of the water used in making up the solution; D is a constant analogous to A ; E is a constant, equal to $F - A$, and the constant F is analogous to C .

It thus appears that the simple suppositions which we have made as to the constitution of electrolytic solutions lead to the formulas for the heat capacity and the volume of solutions which have been shown to represent the results of observation.

7. *Formulas of Mathias and of Tammann.*—Of the formulas which have heretofore been proposed to represent the heat capacities or the specific heats of solutions, it is worth while to notice those of Mathias and of Tammann.

Mathias¹ proposed a formula for the specific heats, with two

¹ Journal de Physique, Vol. 8, p. 204.

constants, a and b , of the form

$$\gamma_n = \frac{a + n}{b + n} c;$$

in which γ_n is the specific heat of the solution containing n gram equivalents of the solvent, and c is the specific heat of the solvent. This formula sometimes represents the specific heats given by Thomsen and by Marignac exceeding well. In other cases it is not so successful. In his notice in the *Comptes Rendus*, 107, p. 524, Mathias presents his results for sodium chloride and hydrochloric acid solutions as examples of the applicability of his formula. In the following table his results are compared with Thomsen's observations and with the values given by the formula presented in this paper.

<i>N</i>	NaCl			HCl		
	<i>H Obs. Th.</i>	<i>H Calc. Mat</i>	<i>H Calc. M</i>	<i>H Obs. Th.</i>	<i>H Calc. Mat</i>	<i>H Calc. M</i>
20	361	359	361	339	338.2	339.6
30	536	534.5	536.1			
50	892	890.6	892.2	873	873.8	872.4
100	1,788	1,786.2	1,788	1,770	1,772	1,769.6
200	3,585 ¹	3,584	3,584.4	3,567	3,571	3,568

These tables show that the formula of Mathias, in which the concentration, as represents by n , is taken as the variable upon which the change of specific heat depends, does not represent the observations so exactly as the formula in which the dissociation is the variable.

Tammann² considers the peculiarities of the heat capacities of solutions to result from the change in the heat capacity of the solvent, due to an internal pressure caused by the presence of the solute. His main principle is like that upon which the formula presented in this paper is based, except that he considers the internal pressure as affecting the whole mass of solution. As might be expected from the difficulty of obtaining the data which he needs for his computations, Tammann's calculated heat capacities do not represent the observations with any accuracy.

¹ Corrected by smoothing the curves of specific heat.

² *Zeitschrift für Phys. Chem.*, Vol. 18, p. 625.

8. *Formulas for Non-electrolytic Solutions.* — In the case of solutions which are not electrolytes, in which, therefore, p is equal to zero or is negligibly small, the formula for the heat capacities reduces to the sum of two terms, of which the first represents the heat capacity of the water and the second is a constant characteristic of the solute. Such a formula has been shown¹ to represent the heat capacity of many non-electrolytic solutions. In cases in which it does not do so, as in the case of the solutions of the alcohols in water, other considerations, notably the heat developed on solution, lead us to conclude that an interaction takes place between the solvent and the solute of a nature similar in general to that supposed to occur in the cases of the electrolytes. The laws of this interaction are not known, and I have not been able to find a formula which will adequately represent the results of observation in these exceptional cases.

In the normal cases, in which the simple additive formula for the heat capacity applies, a similar formula holds for the volumes of the solutions. This has been shown by Wade and by Wanklyn² for solutions of cane sugar, and calculations from the data given by various observers for the volumes of solutions of dextrose, of levulose, of urea, and of glycerine, chosen as typical examples, show that the volumes of solutions of these substances obey the same law. In the tables given by Traube³ several other examples of the same law appear.

9. *Apparent Heat Capacities and Volumes of Ions.* — The range of observation within which our formulas, especially the one for the heat capacity, can be tested, is not very great, and it is desirable to have further confirmation of our hypothesis than that afforded by the agreement between calculated and observed results shown in the tables. This may be obtained from the following considerations:

In the construction of the general formula to which both the heat capacities and the volumes conform, the ions formed by dissociation were considered together, the symbols σ and α being in a way composite quantities, expressing the action of all the ions. It is, how-

¹ Magie, this REVIEW, IX., p. 65; XIII., p. 91.

² Phil. Mag., June-Dec., 1891, p. 475.

³ Liebig's Ann., 290, p. 43.

ever, possible, by introducing separate symbols for the ion of each sort, to write out the term C as the sum of similarly formed terms referring to each ion. Indicating these terms by subscripts 0 and 1 in the case of a simple binary electrolyte, like sodium chloride, C becomes

$$\sigma_1 m_1 + \sigma_1 a_1 M - S a_1 M + \sigma_0 m_0 + \sigma_0 a_0 M - S a_0 M.$$

If now we have another binary electrolyte, like potassium chloride, containing the ion indicated by the subscript 0 and another indicated by a subscript 2, the C for that substance becomes

$$\sigma_2 m_2 + \sigma_2 a_2 M - S a_2 M + \sigma_0 m_0 + \sigma_0 a_0 M - S a_0 M.$$

The difference between these quantities is independent of the common ion, and we should therefore expect to find their difference the same, say for the sodium and potassium compounds, whatever the common ion may be.

A similar relation may be expected to hold among the values of F relating to the volumes of the solutions.

This expectation is fairly well met in the cases of the simpler solutions, in which we have no reason to suspect that there is more than one type of dissociation. For the sodium and potassium compounds we have the following values of C and F , and of their respective differences :

Solution.	C	Diff.	F	Diff.
NaCl	-31	22	13.9	-8.1
KCl	-53		22	
NaOH	-33.6	17.4	-8	-9
KOH	-51		1	
NaNO ₃	-20	22	24	-11.5
KNO ₃	-42		35.5	

Similarly the difference of the constants C referring to the chlorine and NO₃ ions is the same for either sodium or potassium chloride and nitrate and for barium chloride and nitrate.

Solution.	C	Diff.	Solution.	Diff.	C
NaCl	-31	-11	$\frac{1}{2}$ BaCl ₂	-55	-10
NaNO ₃	-20		$\frac{1}{2}$ Ba(NO ₃) ₂	-45	

A much larger collection of data than I have been able to obtain is needed to prove that these differences are generally constant, and the matter is so complicated by the probability that more than one type of dissociation occurs in most of the available solutions, that exceptions to the rule are rather to be expected than not. Such complicated dissociations occur with the barium and strontium compounds and may account for the failure of their solutions to follow the rule to which the simpler solutions of the sodium and potassium compounds conform.

Similar differences, and interpreted in a similar manner as the differences of the effective volumes in solution of two different ions, have been discovered and fully discussed by Traube.¹

10. *Apparent Change of the Heat Capacity of the Water Associated with the Ions.* — By proceeding upon our hypothesis a relation can be deduced from the constant C for the different solutes examined, which may serve as an additional confirmation of the hypothesis. This constant represents the heat capacity of a gram-molecule of the dissociated solute and of the water associated with it, diminished by the heat capacity of the water when not in association with the ions. If we suppose that the ions of the solute retain the heat capacities which they have as atoms, which is practically the same thing as giving to the dissociated molecule its heat capacity when in the solid state — or, if this is not known, making up a heat capacity for it by adding the atomic heats of its atoms as determined by Kopp — we then find the amount by which the heat capacity of the water associated with the dissociated molecule is diminished by subtracting its heat capacity from the value of C in each case. When this is done, the numbers obtained, with one or two exceptions, fall into two groups, which are presented in the following tables. The

	C	h	$C-h$		C	h	$C-h$
NaCl	-31	12.5	-43.5	KCl	-53	12.8	-65.8
NH ₄ Cl	-23.1	20.9	-44	KNO ₃	-42	24.1	-66.1
NaNO ₃	-20	23.6	-43.6	KOH	-51	13.3	-64.3
NaOH	-33.6	13.3	-46.9	$\frac{1}{2}$ BaCl ₂	-55	9.4	-64.4
HCl	-37	8.8	-45.8	$\frac{1}{2}$ SrCl ₂	-59.4	9.5	-68.9
				$\frac{1}{2}$ Ba(NO ₃) ₂	-45	19.9	-64.9
		Mean - 44.8				Mean - 65.7	

¹ Zeitschrift für anorg. Chem., 3, p. 11.

symbol h represents the heat capacity of the molecule of solute. The values for $\frac{1}{2}\text{H}_2\text{SO}_4$ and for $\frac{1}{2}\text{Sr}(\text{NO}_3)_2$ do not fall into either of these groups. In the case of the sulphuric acid, this can be accounted for by the mode of dissociation.

Viewed in the light of our hypothesis, these results indicate that the influence of ions of various sorts upon the water molecules which surround them, though not always the same, is practically the same in many cases. It is noticeable that the sodium compounds are all in one group, the potassium compounds in the other.

If we assume that each water molecule is equally affected by the ion with which it is connected, we may use these numbers to obtain an inferior limit to the number of water molecules thus affected. The mean loss of heat capacity of the water connected with the ions of the first group is 45, that is 2.5 times the heat capacity of one water molecule. There must therefore be at least three molecules of water affected by the two ions, and that there may be so few, it must be admitted that they lose five sixths their heat capacity. So great a change in heat capacity seems to be out of the question, and one is naturally led to assume that the sphere of influence of each ion contains several water molecules. This assumption, furthermore, is supported by the occasional failure of the formulas to represent the observations for the higher concentrations. The differences between the calculated and observed heat capacities and volumes for the most dilute solutions can be ascribed to experimental errors in determining specific heats and specific gravities; but experimental errors have less influence in the case of the more concentrated solutions, and the differences between the calculated and observed results for those concentrations are no doubt real. They may easily be explained if we consider the spheres of influence of the ions, and of the undissociated molecule, as extending so far as to include groups of water molecules. When the concentration becomes such that these groups interpenetrate, or even come into frequent collision, it may reasonably be expected that their heat capacities and volumes should be altered.

11. *Nature of the Association.* — The association between the water and the solute must be of such a sort as to permit an explanation of the laws of osmotic pressure and of electrolytic conduc-

tion. It does not seem possible to account for these laws, especially for those of conduction, if the association is of such a sort as to form definite hydrates or permanent groups of water molecules around the molecules and ions of the solute. If, however, the groups are not permanent, but are loose and unstable, so that the molecules and ions of the solute can slip along through the water without dragging all the water molecules of the group with them, the way to a kinetic explanation of osmotic pressure is left open, and the different ions may still exhibit their different characteristic velocities, postulated for them in Kohlrausch's theory of electrolytic conduction.

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INDUCTANCE OF STRAIGHT CONDUCTOR.

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I.

THE inductance of a length l of a straight conductor is usually given by the equation

$$L = 2l \lg \frac{D}{r} \times 10^{-9}. \quad (1)$$

Where D = distance of return conductor, r = radius of the conductor and the total length of the conductor is assumed as infinitely great compared with l and D . This is approximately the case with the conductors of a long distance transmission line.

For infinite distance D of the return conductor, that is, a conductor without return conductor, equation (1) gives $L = \infty$, that is, a finite length of an infinitely long conductor without return conductor has an infinite inductance L and so inversely zero capacity C .

In equation (1), the magnetic field is assumed as instantaneous, that is, the velocity of propagation of the magnetic field is neglected. With alternating currents traversing the conductor, this is permissible, when the distance to the return conductor is a negligible fraction of the wave-length. That is, if D is negligible compared with v/N , where v = velocity of light, N = frequency of alternating current. It obviously is not permissible in a conductor having no return conductor.

If a conductor conveying an alternating current has no return conductor, its circuit is closed by electrostatic capacity, either the distributed capacity of the conductor, or capacity connected to the ends of the conductor. To produce in such a case considerable currents, either the conductor must be very long, or the frequency and E.M.F. very high.

No conductor extending parallel to the ground, as a telegraph or transmission wire can be considered as having no return, since

even if the conductor is isolated from the ground, secondary currents induced in the ground (or in the higher regions of the atmosphere) act inductively as return currents.

Hence the case of the conductor without return conductor can physically be realized only by a conductor perpendicular to the ground, as the sending and receiving antennæ of a wireless telegraph station, and even then completely only if there are no other vertical conductors, as trees, mountains, etc., which may act as inductive returns, in the space, that is on the ocean.

Since a vertical conductor is limited in length, very high frequencies are required, and so the wave is of moderate length, that is, the velocity of propagation of the magnetic (and electrostatic) field must be considered in investigating the self-induction and the mutual induction of such a conductor.

That is, the magnetic field at a distance u from the conductor, and at time t , corresponds to the current in the conductor at the time $t - t'$, where t' is the time required for the electric field to travel the distance u , that is, $t' = u/v$, where v = velocity of light. Or: the magnetic field at distance u and time t corresponds to the current in the conductor at the time $t - u/v$.

Representing the time t by angle: $\varphi = 2\pi Nt$, where N = frequency of alternating current in the conductor, and denoting

$$a = \frac{2\pi N}{v} = \frac{2\pi}{\lambda},$$

where :

$$\lambda = \text{wave-length of electric current.} \quad (2)$$

The field at distance u and time angle φ corresponds to time angle $\varphi = au$, that is, lags in time behind the current in the conductor by the phase angle au .

II. SECTION I OF INFINITELY LONG STRAIGHT CONDUCTOR WITHOUT RETURN CONDUCTOR.

Let :

$$i = I \sin \varphi = \text{current, abs. units.} \quad (3)$$

The magnetic induction at distance u then is :

$$B = \frac{2I}{u} \sin (\varphi - au), \quad (4)$$

hence, the total magnetic flux surrounding the conductor, from distance r to infinity :

$$\begin{aligned}\Phi &= l \int_r^\infty \frac{2I}{u} \sin(\varphi - au) du \\ &= 2Il \left\{ \sin \varphi \int_r^\infty \frac{\cos au}{u} du - \cos \varphi \int_r^\infty \frac{\sin au}{u} du \right\} \quad (5)\end{aligned}$$

or, substituting the symbols :

$$\left. \begin{aligned} \int_r^\infty \frac{\cos au}{u} du &= \text{col } ar \\ \int_r^\infty \frac{\sin au}{u} du &= \text{sil } ar \end{aligned} \right\} \quad (6)$$

it is :

$$\Phi = 2Il \{ \sin \varphi \text{col } ar - \cos \varphi \text{sil } ar \}. \quad (7)$$

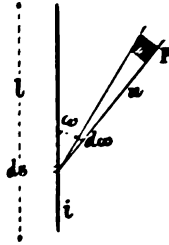


Fig. 1.

The E.M.F. consumed by this magnetic flux, or E.M.F. consumed by self-induction, then is :

$$e = \frac{d\Phi}{d\varphi},$$

hence :

$$e = 2Il \{ \cos \varphi \text{col } ar + \sin \varphi \text{sil } ar \} \quad (8)$$

and since the current is :

$$i = I \sin \varphi,$$

the E.M.F. consumed by self-induction contains an *energy component* :

$$e_1 = 2Il \text{sil } ar \sin \varphi \quad (9)$$

and a *wattless component* :

$$e_2 = 2l\partial \text{col } ar \cos \varphi \quad (10)$$

which latter leads the current by a quarter period.

The energy component e_1 gives rise to an *effective resistance*:

$$r_1 = e_1/i = 2l \operatorname{sil} ar. \quad (11)$$

and a *reactance*:

$$x = \left| \frac{e_2}{i} \right| = 2l \operatorname{col} ar. \quad (12)$$

When considering the finite velocity of propagation of the magnetic field, self-induction is thus not wattless, but contains an energy component, and can be represented by an impedance:

$$\begin{aligned} Z &= r_1 - jx, \\ &= 2l(\operatorname{sil} ar - j \operatorname{col} ar), \\ &= 2l(\operatorname{sil} ar - j \operatorname{col} ar) 10^{-9} \text{ ohms.} \end{aligned} \quad (13)$$

The *inductance* L would then be given by:

$$\begin{aligned} L &= \frac{jZ}{2\pi N}, \\ &= \frac{l}{\pi N} (\operatorname{col} ar + j \operatorname{sil} ar), \\ &= \frac{l}{\pi N} (\operatorname{col} ar + j \operatorname{sil} ar) 10^{-9} \text{ henrys.} \end{aligned} \quad (14)$$

The effective resistance r_1 represents the power

$$P_1 = i^2 r_1, \quad (15)$$

which is sent out by the conductor as electromagnetic radiation.

The functions:

$$\begin{aligned} \operatorname{col} ar &= \int_r^\infty \frac{\cos au}{u} du, \\ \operatorname{sil} ar &= \int_r^\infty \frac{\sin au}{u} du, \end{aligned}$$

or:

$$\left. \begin{aligned} \operatorname{col} y &= \int_r^\infty \frac{\cos y}{y} dy, \\ \operatorname{sil} y &= \int_r^\infty \frac{\sin y}{y} dy, \end{aligned} \right\} \quad (16)$$

can in general not be expressed in finite form, and so would have to be recorded in tables.

In some of the most important cases however, close approximations can be derived of these functions $\text{col } y$ and $\text{sil } y$, in finite form.

III. SELF-INDUCTANCE OF CONDUCTOR.

When considering the reaction of the magnetic field on the conductor, which produces it, if:

l = length of a section of the infinitely long conductor,

r = radius of conductor,

even at extremely high frequency, r is small compared with $1/a$, hence ra a very small quantity, and then $\text{sil } ar$ and $\text{col } ar$ can be approximated.

The integral

$$y' = \int_0^\infty \frac{e^{-bu} \sin au}{u} du, \quad (17)$$

differentiated gives

$$\frac{dy'}{da} = \int_0^\infty e^{-bu} \cos au du. \quad (18)$$

By partial integration, it is:

$$\int e^{-bu} \cos au du = \frac{e^{-bu}(a \sin au - b \cos au)}{a^2 + b^2}.$$

Hence,

$$\frac{dy'}{da} = \frac{b}{a^2 + b^2}$$

and

$$y' = b \int \frac{da}{a^2 + b^2} + C = \tan^{-1} \left(\frac{a}{b} \right) + C. \quad (19)$$

But y' and $\tan^{-1}(a/b)$ vanish with $a = 0$ and we get $C = 0$.

The integral (17) becomes

$$y' = \int_0^\infty \frac{e^{-bu} \sin au}{u} du = \tan^{-1} \left(\frac{a}{b} \right). \quad (20)$$

In the limit case of $b = 0$, we get

$$y'' = \int_0^\infty \frac{\sin au}{u} du = \frac{\pi}{2}. \quad (21)$$

If in the integral:

$$y''' = \int_0^r \frac{\sin au}{u} du. \quad (22)$$

r is a very small quantity, expanding the sine function into a series and integrating the series, gives :

$$y''' = \int_0^r \frac{1}{u} \left(au - \frac{a^3 u^3}{3} + \frac{a^5 u^5}{5} \dots \right) du$$

hence :

$$y''' = ar - \frac{a^3 r^3}{3 \cdot 3} + \frac{a^5 r^5}{5 \cdot 5} \dots \quad (23)$$

Combining (21) and (23), we get

$$\int_r^\infty \frac{\sin au}{u} du = y'' - y''' = \frac{\pi}{2} - ar + \frac{a^3 r^3}{3 \cdot 3} - \frac{a^5 r^5}{5 \cdot 5} + \dots \quad (24)$$

In integral calculus, we have the relation between these two definite integrals

$$\int_\delta^\gamma \frac{\cos a\theta}{\sin \frac{1}{2}\theta} d\theta = 2 \int_{a\delta}^{a\gamma} \frac{\cos \varphi}{\varphi} d\varphi,$$

provided that $\gamma > \delta$, $a\gamma = \infty$ and γ and δ are very small.

From trigonometry, we get

$$\begin{aligned} 2 \{ \sin \theta + \sin 2\theta + \dots + \sin S\theta \} &= \frac{2 \sin \frac{1}{2}(1+S)\theta \cdot \sin \frac{1}{2}S\theta}{\sin \frac{1}{2}\theta} \\ &= \frac{\cos \frac{1}{2}\theta - \cos (\frac{1}{2} + S)\theta}{\sin \frac{1}{2}\theta}. \end{aligned}$$

Integrating this equation, we get

$$\begin{aligned} \int_\delta^\pi \frac{\cos (\frac{1}{2} + S)\theta}{\sin \frac{1}{2}\theta} d\theta &= \int_\delta^\pi \cot \frac{1}{2}\theta d\theta \\ &\quad + 2 \left[\cos \theta + \frac{1}{2} \cos 2\theta + \dots + \frac{1}{S} \cos S\theta \right] \\ &= 2 \lg \frac{\sin \frac{\pi}{2}}{\sin \frac{\delta}{2}} + 2 \left(-1 + \frac{1}{2} - \frac{1}{3} + \dots + \frac{(-1)^S}{S} \right) \\ &\quad - 2 \left(\cos \delta + \frac{1}{2} \cos 2\delta + \dots + \frac{1}{S} \cos S\delta \right) \end{aligned}$$

or

$$\int_\delta^\pi \frac{\cos (\frac{1}{2} + S)\theta}{\sin \frac{1}{2}\theta} d\theta = -2 \left\{ 1 - \frac{1}{2} + \frac{1}{3} - \dots - \frac{(-1)^S}{S} - \lg 2 \right\}$$

$$- 2 \lg \frac{2 \sin \frac{\delta}{2}}{\delta} - 2 \lg S \delta + 2 \left\{ \lg S - 1 - \frac{1}{2} - \frac{1}{3} - \dots - \frac{1}{S} \right\} \\ + 2 \left\{ 1 + \frac{1}{2} + \frac{1}{3} + \dots + \frac{1}{S} - \left(\cos \delta + \frac{1}{2} \cos 2\delta + \dots + \frac{1}{S} \cos S\delta \right) \right\}.$$

Now let us increase S infinitely great, and $S\delta$ remaining finite, so that δ decreases infinitely small, this combined with the preceding equation, gives

$$\text{Limit}_{S=\infty} \int_{\delta}^{\pi} \frac{\cos(\frac{1}{2} + S)\theta}{\sin \frac{1}{2}\theta} d\theta = 2 \int_{S\delta}^{S\pi} \frac{\cos \varphi}{\varphi} d\varphi = - 2 \lg S \delta \\ + 2 \left\{ \lg S - 1 - \frac{1}{2} - \frac{1}{3} \dots - \frac{1}{S} \right\} \\ + 2 \left\{ \left[\frac{\delta^2}{2} + \frac{(2\delta)^2}{2 \cdot 2} + \dots + \frac{(S\delta)^2}{S \cdot 2} \right] - \left[\frac{\delta^4}{4} + \frac{(2\delta)^4}{2 \cdot 4} + \dots \right] + \dots \right\},$$

or

$$\text{Limit}_{S=\infty} \int_{S\delta}^{S\pi} \frac{\cos \varphi}{\varphi} d\varphi = - \lg S \delta - \left\{ \left(1 + \frac{1}{2} + \frac{1}{3} + \dots + \frac{1}{S} \right) - \lg S \right\} \\ + \frac{(S\delta)^2}{2 \cdot 2} - \frac{(S\delta)^4}{4 \cdot 4} + \dots$$

Let us denote the second term of the above expression by q , or

$$q = \text{Limit}_{S=\infty} \left\{ \sum_1^S \frac{1}{S} - \lg S \right\}.$$

This series has a finite value and has been computed to be

$$0.5772156 \dots$$

Putting $S\delta = d$ and $S\pi = \infty$, we get

$$\int_d^{\infty} \frac{\cos \varphi}{\varphi} d\varphi = - q - \lg d + \frac{d^2}{2 \cdot 2} - \frac{d^4}{4 \cdot 4} + \dots$$

Hence, we obtain

$$\int_r^{\infty} \frac{\cos au}{u} du = - q - \lg ar + \frac{(ar)^2}{2 \cdot 2} - \frac{(ar)^4}{4 \cdot 4} + \dots \quad (25)$$

Combining the results obtained in (24) and (25), we get

$$\begin{aligned} \Phi = 2Il \left\{ \sin \varphi \cdot \left(-q - lg ar + \frac{(ar)^2}{2 \cdot 2} - \frac{(ar)^4}{4 \cdot 4} + \dots \right) \right. \\ \left. - \cos \varphi \cdot \left(\frac{\pi}{2} - ar + \frac{(ar)^3}{3 \cdot 3} - \frac{(ar)^5}{5 \cdot 5} + \dots \right) \right\}. \quad (26) \end{aligned}$$

With the dimension of common wire, we can neglect all terms containing ar except $lg ar$, and we have

$$\Phi' = -2Il \left\{ (q + lg ar) \cdot \sin \varphi + \frac{\pi}{2} \cos \varphi \right\}, \quad (27)$$

or

$$\Phi' = -2Il \sqrt{(q + lg ar)^2 + \frac{\pi^2}{4}} \sin(\varphi - \omega), \quad (28)$$

where

$$\tan \omega = \frac{\pi}{2(q + lg ar)} \quad (29)$$

and

$$q = 0.5772156 \dots \quad (30)$$

Therefrom follows: (13)

$$\begin{aligned} Z &= 2l \left\{ \frac{\pi}{2} + j(q + lg ar) \right\} 10^{-9} \\ &= 2l \left\{ \frac{\pi}{2} - j \left(lg \frac{1}{ar} - q \right) \right\} 10^{-9} \text{ ohms} \quad (31) \end{aligned}$$

and, (14)

$$\begin{aligned} L &= \frac{l}{\pi N} \left\{ -(q + lg ar) + j \frac{\pi}{2} \right\} 10^{-9} \\ &= \frac{l}{\pi N} \left\{ \left(lg \frac{1}{ar} - q \right) + j \frac{\pi}{2} \right\} 10^{-9} \text{ henrys} \quad (32) \end{aligned}$$

as the effective impedance, and inductance, respectively, of a section l of an infinitely long conductor at frequency N , where:

$$a = \frac{2\pi N}{v}$$

and

$$\begin{aligned} v &= \text{velocity of light.} \\ q &= .5772156 \dots \end{aligned}$$

It follows herefrom :

The power radiated by the conductor, section l , as electromagnetic wave :

$$\begin{aligned} P &= i^2 r_1 \\ &= 2l \frac{\pi}{2} i^2 \\ &= \pi l i^2 \end{aligned} \quad (33)$$

is independent of the frequency N , and the conductor dimensions, as the radius r , as long as ar is negligible, that is, $2\pi Nr$ small compared with the velocity of light v , or $2\pi r$ small compared with the wave-length λ .

Instance :

$$l = 200 \text{ ft} = 6,000 \text{ cm.}$$

$$r = .4'' = 1 \text{ cm.}$$

$$N = 400,000 \text{ cycles,}$$

hence

$$\lambda = 2500 \text{ ft.}$$

$$ar = 85 \times 10^{-6}$$

and

$$Z = (18.9 - 105.5j) 10^{-6} \text{ ohms.}$$

At

$$i = 1000 \text{ amps.}$$

$$P = 18.9 \text{ watts.}$$

IV. SELF-INDUCTANCE OF STRAIGHT CONDUCTOR OF FINITE LENGTH l .

Let

$$i = I \sin \varphi = \text{current.}$$

$$l = \text{length of the wire.}$$

$$a/2\pi N = \text{reciprocal of the velocity of the propagation of the electromagnetic wave.}$$

$$ds = \text{equivalent current element on the axis of the wire.}$$

$$u = \text{vector drawn from } ds \text{ to the point } P \text{ outside the wire.}$$

$$\omega = \text{the angle between the vector } u \text{ and the current } i.$$

The magnetic induction due to the current element at any point in free space is represented by

$$B = \frac{I \sin(\varphi - au) \cdot \sin \omega \cdot ds}{u^2}.$$

The total flux of magnetic induction around the wire is given by the following integral

$$\phi = \int_0^L \int_0^\pi \int_{r/\sin \omega}^\infty \frac{I \sin(\varphi - au) \cdot u \cdot \sin \omega}{u^2} du d\omega ds \quad (34)$$

or

$$\phi = I \int_0^L \int_0^\pi \int_{r/\sin \omega}^\infty \frac{\sin(\varphi - au) \cdot \sin \omega}{u} du d\omega ds. \quad (35)$$

The first integral of the above equation is just the same form as treated in the preceding case, and we have

$$\phi = I \int_0^L \int_0^\pi \left\{ \sin \varphi \cdot [-q - lg ar + lg(\sin \omega)] - \cos \varphi \cdot \frac{\pi}{2} \right\} \sin \omega d\omega ds. \quad (36)$$

Consider the integral

$$\int_0^\pi \sin \omega \cdot lg(\sin \omega) d\omega,$$

we have

$$X \equiv \int_0^\pi \sin \omega \cdot lg(\sin \omega) d\omega = 2 \int_0^{\pi/2} \sin \omega \cdot lg(\sin \omega) d\omega$$

and

$$Y \equiv \int \sin \omega \cdot lg(\sin \omega) d\omega = \cos \omega - \cos \omega \cdot lg(\sin \omega) + \frac{1}{2} lg \frac{1 - \cos \omega}{1 + \cos \omega}.$$

Hence, we obtain

$$X = 2L \lim_{\epsilon=0} [Y]_{\pi/2}^{\pi/2} = 2L \lim_{\epsilon=0} \left\{ lg 2 - 1 + \left(lg \frac{\epsilon}{2} - lg \frac{\epsilon}{2} \right) \right\} = 2(lg 2 - 1),$$

or

$$\int_0^\pi \sin \omega \cdot lg(\sin \omega) d\omega = 2(lg 2 - 1).$$

Consequently, we get

$$\phi = 2I \int_0^L \left\{ -(q + lg ar + 1 - lg 2) \sin \varphi - \frac{\pi}{2} \cos \varphi \right\} ds,$$

or

$$\begin{aligned}\phi &= 2\pi \left\{ \left(lg \frac{1}{ar} - q - 1 + lg 2 \right) \sin \varphi - \frac{\pi}{2} \cos \varphi \right\} \\ &= 2\pi \left\{ \left(lg \frac{1}{ar} - s \right) \sin \varphi - \frac{\pi}{2} \cos \varphi \right\}\end{aligned}\quad (37)$$

where

$$s = q + 1 - lg 2 = .8841 \dots$$

or

$$\phi = 2\pi \sqrt{\left(lg \frac{1}{ar} - s \right)^2 + \left(\frac{\pi}{2} \right)^2} \sin(\varphi - \omega) \quad (38)$$

where

$$\tan \omega = \frac{\pi}{2 \left(lg \frac{1}{ar} - s \right)} \quad (39)$$

hence

$$Z = 2l \left\{ \frac{\pi}{2} - j \left(lg \frac{1}{ar} - s \right) \right\} 10^{-9} \text{ ohms}, \quad (40)$$

and

$$L = \frac{l}{\pi N} \left\{ \left(lg \frac{1}{ar} - s \right) + j \frac{\pi}{2} \right\} 10^{-9} \text{ henrys}. \quad (41)$$

Instance :

Length of conductor, $l = 200 \text{ ft.} = 6000 \text{ cm.}$

Diameter of conductor, $2r = .8'' = 2 \text{ cm.}$

Conductor grounded at bottom, connected at top to capacity about three times that of the conductor, so as to reduce its frequency of oscillation to $N = 400,000$ cycles. This gives $Z = (18.9 - 102j)10^{-6}$ ohms. At $i = 1,000$ amps., $P = i^2 r_1 = 18.9$ watts.

V. MUTUAL INDUCTANCE BETWEEN TWO FINITE STRAIGHT CONDUCTORS AT CONSIDERABLE DISTANCE FROM EACH OTHER.

This problem is of interest in relation to wireless telegraphy, in that it investigates one component, the electromagnetic, of the electric field which transmits the message between sending and receiving station.

The distance between the two conductors is supposed to be very great compared with the lengths of the wires, and the angles subtended by one of the wires to any point in another wire may be considered equal to each other.

Let :

l and l_1 = lengths of the straight conductors in space.

D = length of any vector connecting the wires.

α and α_1 = angles between D and the wires.

As we have assumed D to be very great compared with l and l_1 , the angles α and α_1 may be considered remain constant independent of D .

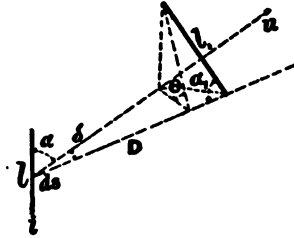


Fig. 2.

Also, let us denote by δ the angle subtended by any point in l_1 carrying electric current i to the projection of l_1 upon the plane determined by l and D ; and θ the angle between the planes determined by the vector D and each of the wires l and l_1 .

The projection of l_1 upon the plane of l and D can be decomposed into two components, one parallel to and another perpendicular to the vector D ; thus, we get

$$l_1 \cos \alpha_1 = \text{parallel component.}$$

$$l_1 \sin \alpha_1 \cos \theta = \text{normal component.}$$

$$\delta = \frac{l_1 \sin \alpha_1 \cos \theta}{D}.$$

Hence, we get the following integral for the expression of the total flux of the magnetic induction which has just passed over the conductor l_1 at the instant t .

$$\phi = \int_0^l \int_D^\infty \frac{I \sin (2\pi Nt - au) \cdot \sin \alpha \cdot u \cdot \delta}{u^2} du ds$$

or

$$\phi = \frac{Il_1 \sin \alpha_1 \sin \alpha \cos \theta}{D} \int_0^l \int_D^\infty \frac{\sin (\varphi - au)}{u} du ds.$$

Let us suppose that the distance D is very great compared with the lengths of conductors l and l_1 and the wave-length λ .

Putting $D = \lambda(m + s)/4$, where m is a large positive integer and s the positive fractional part less than one, we have

$$\begin{aligned} X &= \int_0^\infty \frac{\sin(\varphi - au)}{u} du \\ &= \int_0^\infty \frac{\sin \varphi \cos au}{u} du - \int_0^\infty \frac{\cos \varphi \sin au}{u} du \\ &= \sin \varphi \left[\int_0^{\lambda(m+1)/4} + \int_{\lambda(m+1)/4}^{\lambda(m+2)/4} + \dots \right] \frac{\cos au}{u} du \\ &\quad - \cos \varphi \left[\int_0^{\lambda(m+1)/4} + \int_{\lambda(m+1)/4}^{\lambda(m+2)/4} + \dots \right] \frac{\sin au}{u} du \end{aligned}$$

(i) $m = 2n$

$$\begin{aligned} X_1 &\doteq (-1)^n \left(1 - \sin \frac{s\pi}{2} \right) \frac{\sin \varphi}{\frac{\lambda}{4}na} + (-1)^n \left(1 - \cos \frac{s\pi}{2} \right) \frac{\cos \varphi}{\frac{\lambda}{4}(2n+1)a} \\ &\quad - (-1)^n \frac{\sin \varphi}{\frac{\lambda}{4}a} \left\{ \frac{1}{n+1} - \frac{1}{n+2} + \frac{1}{n+3} \dots \right\} \\ &\quad - (-1)^n \frac{\cos \varphi}{\frac{\lambda}{4}a} \left\{ \frac{1}{n+\frac{1}{2}} - \frac{1}{n+1+\frac{1}{2}} + \frac{1}{n+2+\frac{1}{2}} \dots \right\}. \end{aligned}$$

(ii) $m = 2p + 1$

$$\begin{aligned} X_{11} &\doteq (-1)^p \frac{\sin \varphi}{\frac{\lambda}{4}(2p+2)a} \left(1 - \sin \frac{s\pi}{2} \right) \\ &\quad + (-1)^p \frac{\cos \varphi}{\frac{\lambda}{4}(2p+1)a} \left(1 - \cos \frac{s\pi}{2} \right) \\ &\quad - (-1)^p \frac{\sin \varphi}{\frac{\lambda}{4}a} \left\{ \frac{1}{p+1} - \frac{1}{p+2} + \dots \right\} \\ &\quad + (-1)^p \frac{\cos \varphi}{\frac{\lambda}{4}a} \left\{ \frac{1}{p+1+\frac{1}{2}} - \frac{1}{p+2+\frac{1}{2}} + \dots \right\}. \end{aligned}$$

These results have already a relative error of $(\lambda/4D)^2$ order and the summation of the fractional series can be obtained only in approximate ways.

It can be shown that the summation of the series,

$$S = \frac{1}{n} - \frac{1}{n+1} + \frac{1}{n+2} - \frac{1}{n+3} + \dots = \sum_{p=0}^{\infty} \frac{(-1)^p}{n+p},$$

can be represented by $\frac{1}{4} \log (n^2 - 1)/n(n-2)$ with a relative error of $(1/n)^3$ order.

For the sake of simplicity, we shall follow another method of the approximate calculation.

Let us consider the following series

$$S_0 = \frac{1}{n} - \frac{1}{n+1} + \frac{1}{n+2} \dots$$

$$S' = \frac{1}{n+1} - \frac{1}{n+2} + \frac{1}{n+3} \dots,$$

then we have the following relations

$$S > S'$$

$$S > \frac{1}{(n+1)^2} + \frac{1}{(n+3)^2} + \frac{1}{(n+5)^2} + \dots$$

$$S' < \frac{1}{(n+1)^3} + \frac{1}{(n+3)^3} + \frac{1}{(n+5)^3} + \dots$$

$$S < \frac{1}{n^2} + \frac{1}{(n+2)^2} + \frac{1}{(n+4)^2} + \dots$$

$$\therefore S - S' < \frac{1}{n^2},$$

moreover we have

$$S + S' = \frac{1}{n}.$$

Therefore, neglecting the small quantity $(1/n)^2$, we get

$$S \doteq \frac{1}{2n}.$$

Substituting this approximate result in the preceding equations, we get the generalized formulæ

$$\int_{D=\lambda(m+S)/4}^{\infty} \frac{\sin(\varphi - au)}{u} du \doteq -(-1)^m \frac{\cos(\varphi - aD)}{aD + \pi/2}.$$

Hence, we get

$$\Phi \doteq (-1)^{m+1} \frac{III_1 \sin \alpha \sin \alpha_1 \cos \theta}{D(aD + \pi/2)} \cos(\varphi - aD)$$

where

$$D = \frac{\lambda}{4}(m + s) \text{ and } 0 < s < 1$$

and the formula shall give the result with a relative error of $(1/m)^2$ order.

Taking the differential coefficient of Φ with respect to t , we obtain the expression for the induced E.M.F.

$$e = -\frac{d\Phi}{dt} \doteq (-1)^{m+1} \frac{2\pi N III_1 \sin \alpha \sin \alpha_1 \cos \theta}{D(Da + \pi/2)} \sin(\varphi - aD),$$

or

$$e \doteq (-1)^{m+1} \frac{v III_1 \sin \alpha \sin \alpha_1 \cos \theta}{D\left(D + \frac{\lambda}{4}\right)} \sin \frac{2\pi}{\lambda}(vt - D),$$

where v is the velocity of the propagation of the electromagnetic wave in the air and λ the wave-length.

Writing the equation in another form, we get

$$e \doteq (-1)^{m+1} \left(1 - \frac{\lambda}{4D}\right) \frac{v III_1 \sin \alpha \sin \alpha_1 \cos \theta}{D^2} \sin \frac{2\pi}{\lambda}(vt - D).$$

Instances:

$$l = l_1 = 200 \text{ ft.} \doteq 6100 \text{ cm.}$$

$$r = .4 \text{ inch} \doteq 1 \text{ cm.}$$

$$N = 4 \times 10^5.$$

$$I/\sqrt{2} = 1000 \text{ amp.}$$

$$D_1 = 10 \text{ miles} = 1.61 \times 10^6 \text{ cm.}$$

$$D_2 = 200 \text{ miles} = 3.22 \times 10^7 \text{ cm.}$$

$$D_3 = \text{Quadrant of the earth} \doteq 6214 \text{ miles} \doteq 10^9 \text{ cm.}$$

The induced E.M.F. become

$$(i) \quad \frac{E_1}{\sqrt{2}} = 0.427 \text{ volt.}$$

$$(ii) \quad \frac{E_2}{\sqrt{2}} = 1.08 \text{ millivolts.}$$

$$(iii) \quad \frac{E_s}{\sqrt{2}} = 1.12 \text{ microvolts.}$$

The preceding investigation applies only to the electromagnetic component of the electric field of a straight conductor. Similar equations, however, would be derived in an analogous manner for the electrostatic component of the electric field, that is, for the capacity.

From the relation between the inductance L and the capacity C of a finite length l of an infinitely long conductor.

$$LC = \frac{l^2}{v^2}$$

where v = velocity of light; it follows, that when neglecting the velocity of propagation of the electric field in space, the capacity of a finite length of an infinitely long conductor without return conductor equals zero :

$$C = 0$$

since :

$$L = \infty .$$

Considering the finite velocity of propagation of the electric field in space, L becomes finite, but a function of the frequency of the alternating current, and so the capacity C also becomes finite, and a function of the frequency, which may be evaluated by a similar investigation.

A STUDY OF THE PROPAGATION AND INTERCEPTION OF ENERGY IN WIRELESS TELEGRAPHY.
PART I.

BY CHARLES A. CULVER.

PURPOSE.

FROM time to time our own and various foreign governments have issued numerous patents covering various types of antennæ or aerial systems, which have been designed for the purpose of radiating or receiving electromagnetic waves. While there has been some quantitative work done on the efficiency of these various types, the investigations have been conducted largely along commercial lines. The writer is not aware that any extended quantitative research in this direction has been carried out under conditions permitting of delicate and highly accurate measurement. Aside from the practical bearing which the results of such a research might have, it was believed that a study of the action of these various types might possibly yield data which would throw some light upon one or more of the undetermined theoretical problems at present existing in this field. With this end in view it was *the purpose of this investigation to make a study of the relative efficiency of several different types of receiving systems when used under various conditions.* In so far as this paper treats of aërials or antennæ it has to do with conditions at the receiving station only. In a future paper we hope to investigate several radiating systems in a similar manner.

APPARATUS EMPLOYED.

Sending Station. — The equipment at the power station consisted of a transformer, T , Fig. 1, a , two inductance coils, L_1 and L_2 , a spark gap, G_1 and a battery of six Leyden jars, C_1 . A single insulated wire¹ ten meters in length served as a radiating system.

¹ Whenever wire is referred to hereafter, unless otherwise specified, insulated copper wire No. 10 bearing the trade name "Fire and Water Proof" is meant.

Seven and eight tenths meters of this wire were supported in vertical position by means of a specially constructed high tension insulator. The transformer employed was rated to deliver 25,000 volts when operating on a 104 volt 60 cycle circuit. The voltage, however, was cut down to about 5,000 by means of an adjustable rheostat in

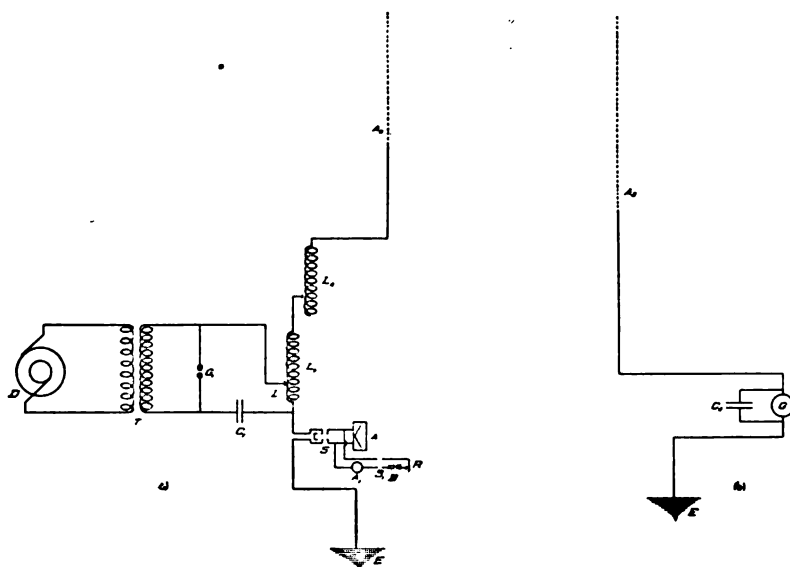


Fig. 1.

series with the primary. Power was secured from commercial mains. The Leyden jars composing the capacity, C_1 , were specially constructed for high tension work and were worked in parallel, their combined capacity being 0.00837 M-F. The two inductance coils, L_1 and L_2 , consisted of 23 turns of No. 9 bare copper wire (B.S.G.) wound on rectangular wooden frames 30.5 cm. square, the pitch of the winding, being 1.3 cm. One of these coils, L_1 , served as an auto-transformer and the other, L_2 , as an auxiliary tuning coil. The spark gap, G_1 , was located on the top of the coil, L_1 , and consisted of two extremely hard and highly polished steel balls 2.54 cm. in diameter, resting on the top of two short upright pieces of brass tubing 1.3 cm. internal diameter. One of these brass supports was adjustable, thus permitting the length of the spark gap to be varied. A spark length of 1 or 2 mm. was employed. Such an

arrangement is probably as satisfactory as any form of gap for the reason that such steel balls are very refractory and may be readily changed or polished. Signals were made by opening and closing a switch in the primary circuit of the transformer, *T*. The power in the commercial mains from which our energy supply was taken varied between 3 and 4 per cent. in voltage. Various forms of earth connections were tried and the one ultimately employed was not used because it permitted the greatest amount of energy to be radiated from the sending station, for it did not, but for other reasons which will become obvious as we proceed. A hole $2 \times 4 \times 6$ feet was excavated in the earth. In the bottom of this hole a piece of gas pipe, 6 feet long, was driven until but 2 or 3 inches remained above the bottom of the hole. A sheet of galvanized iron 2×8 feet, having a hole in the middle large enough to admit the gas pipe, was placed in the excavation. This covered the bottom of the hole and extended upward on either of two sides for some 2 or 3 feet. The gas pipe passed through the hole in the middle of the metal sheet, extending above the same for 2 or 3 inches. Bare copper wire No. 9 (B.S.G.) led from the auto-transformer to earth, being soldered to the plate and also to the pipe. Such an arrangement was found to work reasonably well, though not so satisfactorily as a "ground" made by soldering the earth wire to gas or water pipes in the building. Both the ground and antenna wires were led out of the building through heavy porcelain insulators.

In order to determine when the two oscillating systems at the sending station were in resonance with each other, a specially constructed hot-wire ammeter was inserted between the inductance, L_1 , and the earth. Fleming and others have pointed out that the ordinary commercial hot-wire ammeter will not give correct readings when operating on a high frequency circuit. This is due of course to the fact that with any instrument operating upon the shunt principle, the amount of current which will pass through the instrument proper is a function of the frequency. Since in the process of bringing two parts of any high frequency alternating circuit into resonance the frequency of one or both of the related circuits changes, therefore an instrument to give correct readings, even though only maximum current is desired, must be independent of the frequency

and wave form. In this investigation an instrument was constructed along the lines suggested by Professor Fleming.¹

Referring to Fig. 2, WW_1 is a No. 34 copper wire 32 cm. long, stretched between two binding posts, BB_1 . This wire is drawn taut by a silk thread, TT_1 , 16 cm. in length, fastened to its middle part

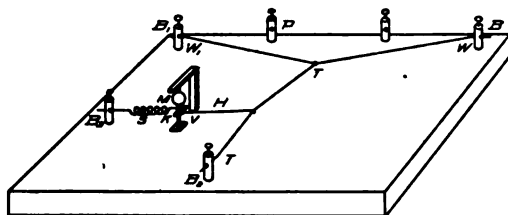


Fig. 2.

by means of a small double hook made of glass, the copper wire slipping freely through the glass hook. The end, T_1 , of the above thread is fastened to a short piece of heavy brass wire which is held in place by a binding post, B_2 . V is a short steel shaft having conical points at either end and supported by suitable brass bearings fastened to the base of the instrument, which is of wood. This shaft carries a mirror, M , fastened to it by any convenient means. The shaft carries a short brass projection, K , having two small holes near its free extremity. A piece of fine piano wire, H , 3 cm. long having a loop at either end connects this brass lever to the middle of the thread, TT_1 . The system thus formed is kept taut by means of spring, S , attached to the brass lever, K , and to a short piece of heavy brass wire which is held in place by means of a binding post, B_3 . Any expansion of the wire, WW_1 , due to current passing through the same will result in a movement of the mirror, M , which may be read by means of telescope and scale in the usual manner. The tension on the wire and the normal position of the mirror is modified by means of the adjustments possible at B_2 and B_3 . A light wooden box enclosed the working parts of the instrument. By suitable choice of the wire, WW , various ranges and degrees of sensibility can be secured. Such an instrument gives the root-mean-square value of the current passing through it, and is independent

¹ The Principles of Electric Wave Telegraphy, p. 142.

of the frequency and wave form. Fig. 3 shows a typical calibration curve of the instrument, made by means of a standard Weston instrument and direct current. A series of tests extending over several days, under varying conditions of temperature and humidity, showed that the instrument held its calibration to a fair degree of accuracy. However, to avoid any possible changes due to external conditions we did not depend upon the calibration curve but used the instrument as a comparator. A reference to Fig. 2 will indicate how this was accomplished. The hot-wire ammeter was so arranged that it

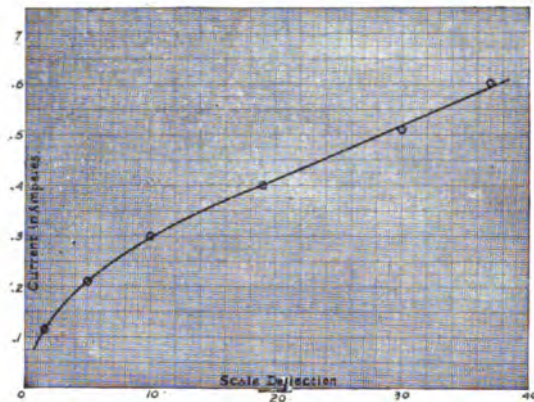


Fig. 3.

could be switched into the oscillating circuit at the same point at all times. After the mean-square value of the oscillating current had been read the ammeter was switched out of the oscillating circuit and into a direct current circuit in series with a finely adjustable rheostat and a standard Weston ammeter. The direct current was then adjusted until a deflection of the hot-wire instrument was secured equal to that caused by the oscillating current. The reading of the Weston instrument then gave the root-mean-square value of the high frequency current. The instrument was utilized not only to determine the conditions of maximum current in the inductance circuit but also to serve as a check on the constancy of the energy output at the sending station whenever it was impracticable to repeat any given set of measurements. After the two circuits at the sending station were brought into resonance the relation of the parts was not changed during the remainder of the experiments.

RECEIVING STATION.

The receiving station was equipped with various forms of antennæ; two adjustable oil condensers, C_2 , arranged in parallel and shunted about the energy-measuring instrument; an oscillating current galvanometer, G , which served to measure the energy intercepted by the various receiving systems; an earth connection, E , similar to that described for the sending station. Fig. 1, *b*, illustrates the connections at the receiving station. The oil condensers consisted of two sets of sectorial-shaped brass plates, one set of which revolved about an axis set near one edge of the movable plates and close to the fixed sectors. A pointer attached to the axis moved over a scale graduated in circular degrees. Several such condensers were at our disposal, having been constructed from plans and specifications given by Clyde C. Swayne in an article which appeared in the *American Electrician* for September, 1905. Each condenser had a maximum capacity of .00211 M-F., and a minimum of .000771 M-F. Such condensers were found to serve admirably for delicate tuning in wireless circuits.

The energy-measuring instrument was an oscillating current galvanometer modelled along the lines suggested by Fleming and developed by Northrup¹ and Pierce.² In general the mechanical construction did not differ materially from the instrument now sold by the Leeds & Northrup Co., except that only one coil was used and the damping magnet was omitted. In detail the instrument as used in this investigation consisted of a small coil composed of 45 turns of No. 36 D.S.C. copper wire wound on a hollow hard rubber bobbin 7 mm. internal diameter. Directly in front of this coil was suspended by a very fine quartz fiber a small silver disc 6 mm. in diameter and .2 mm. thick. The suspension fiber was fastened to the metal disc by shellacing both to a delicate glass stem. The glass stem also carried a tiny mirror. The system thus composed was enclosed in a square hard rubber case having glass windows front and back. The suspension tube was of brass. Brass levelling screws completed the instrument. A non-inductive shunt might have been employed to vary the sensibility of the galvanometer;

¹ *Electrical World*, December 18, 1898.

² *PHYSICAL REVIEW*, Vol. 19, p. 202.

however, only one degree of sensibility was used throughout the experiments. Northrup and Pierce have shown that for small angles the deflection of such an instrument is proportional to the square of the current. The deflections were read by means of telescope and scale placed at a distance of 83 cm. from the galvanometer.

The two stations were 47 meters apart, the sending antenna being located on the north side of one building and the various receiving systems on the south side of an adjacent building, the two buildings constituting the Randall Morgan Laboratory thus being located between the two stations.

WAVE-LENGTH MEASUREMENTS.

In order to measure the two wave-lengths emitted by the transmitting station, a wave-measuring apparatus was set up consisting of one of the adjustable oil condensers before referred to ; a small inductance coil 21 cm. in diameter, carrying 9 turns of low resistance wire ; a Duddell thermo-galvanometer in series with the condenser and inductance.¹ The inductance of the small helix and leads to the same measured by the Fleming-Anderson method was .0642 milli-henrys. This wave-measuring system was set up in the same room with the sending apparatus about 2 m. distant from the same. By means of such an arrangement the wave-length could be measured without the wave-meter circuit exerting any influence upon the system whose wave was being tested. The action of the thermo-galvanometer indicated that it would have been possible to perform the experiment with the wave-meter at even a much greater distance from the transmitting system. The wave-meter circuit was brought into resonance with the sending circuit by adjusting the oil condenser. It was found possible to secure very sharp resonance, a change of .5 of 1 per cent. in the capacity resulting in a falling off of at least 10 per cent. in the current as indicated by the galvanometer. This meant that a change in capacity of nine millionths of

¹ As this investigation is in progress we note the appearance of a paper by Professor Pierce (*PHYSICAL REVIEW*, Vol. 24, p. 152) in which the author describes the use of a similar device for measuring frequencies. Professor Pierce employs an oscillation galvanometer where we use the Duddell instrument. We believe the thermo-galvanometer to be somewhat superior for this purpose in that it is more dead beat and at the same time is amply sensitive for the purpose.

a microfarad was readily detectable. Advantage was taken of this fact later in measuring certain small values of capacity by means of an obvious substitution method. As was to be expected, the galvanometer indicated two current maxima, one with .001464 M-F., another with .001079 M-F.

Fleming has developed the working formula

$$n = \frac{5 \times 10^6}{\sqrt{LC}},$$

where n represents the frequency, L the inductance in centimeters and C the capacity in microfarads. If we substitute in this equation the well-known relation

$$n = \frac{V}{\lambda},$$

where V is the velocity of propagation and λ the wave-length, we obtain the convenient expression

$$\lambda = 6 \times 10^3 \sqrt{LC}.$$

Substituting in this equation the values given above for L and C we get

$$\lambda_1 = 6 \times 10^3 \sqrt{64,200 \times .001464} = 581.7 \text{ meters,}$$

$$\lambda_2 = 6 \times 10^3 \sqrt{64,200 \times .001079} = 499.2 \text{ meters.}$$

Thus it will be seen that the wave-lengths employed were comparable with those used for commercial purposes, the wave-length of the navy being 425 m.

EFFECTS OF EARTH RESISTANCE.

Preliminary Experiments. — During the course of some preliminary experiments conducted at the beginning of this investigation, it was observed that with the receiving apparatus grounded by connecting to a piece of buried wire netting and the sending apparatus grounded to gas or steam pipes, the deflection of the galvanometer was four times what it was when the sending station was grounded to similar pieces of netting. When the receiving station was also grounded to pipes, the transmitting station being earthed through piping, the deflection at the receiving station was ten times what it

was when both stations were earthed to buried netting. If the transmitting station were grounded to the plate and the receiving apparatus grounded first to the plate and then to the pipes in turn, little, if any, difference in the amount of energy received resulted. From these experiments it is apparant that the earth connections play a highly important part in the transmission of energy in wireless telegraph operations, particularly the "ground" at the transmitting station. While this fact is not new such marked differences as those observed when shown by careful measurements led the writer to try some experiments having to do with the effect earth resistance *between* stations might possibly have upon the quantity of energy transmitted. Accordingly the two stations were grounded to the two large galvanized iron earth plates and a wire run between the two stations, connecting to the earth leads where they enter the ground. Between the two stations this wire was insulated from the earth. In series with this wire was an adjustable non-inductive resistance. Thus there was arranged a variable resistance in parallel with the earth. With a constant supply of energy being radiated from the sending station, readings were made at the the receiving station with the parallel-earth-wire *disconnected* at both ends and then again with the variable resistance *connected* in parallel with the earth. While the energy received as shown by the relative deflections of the galvanometer was greater as the earth resistance was decreased, the results were not wholly concordant.

The experiment was next tried of placing several wires between the two stations so arranged that various combinations might be introduced in parallel with the earth. These wires were insulated from the earth except at the points where they connected to the earth leads where these leads entered the ground. To reduce the amount of energy received in order to bring the same within the range of the galvanometer without employing a shunt, a vertical receiving antenna 1.3 m. long was employed. The system thus constituted was brought into resonance with the sending station by adjusting the oil condensers shunted about the galvanometer. (This method of tuning was employed in all the experiments of this research.) By means of a Wheatstone bridge, a buzzer and a telephone the resistance of the earth between the two earth plates

was measured. Similarly the resistance between these two points was measured when 1, 2, 3, . . . 6 wires were in parallel with the earth. Readings were also taken of the relative amounts of energy received under these various conditions. The amount of energy received increased materially as the earth resistance between the two stations was decreased. Table I. embodies the results of this experiment. In Fig. 4 the earth resistance between the two stations is plotted against galvanometer deflection (current square).

TABLE I.

No. of Wires in Parallel with Earth.	Resistance Between Earth Plates, Ohms.	Gal. Deflection (Current Square).	No. of Wires in Parallel with Earth.	Resistance Between Earth Plates, Ohms.	Gal. Deflection (Current Square).
0	90.0	4.0	4	17.0	117.0
1	74.7	38.5	5	14.0	128.0
2	34.7	78.0	6	11.7	140.0
3	22.9	102.0			

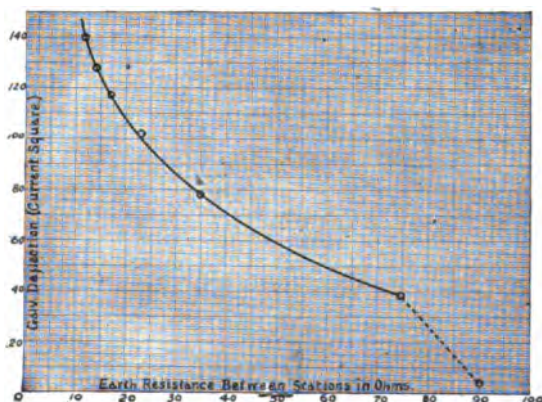


Fig. 4.

To further test the matter of earth resistance the wires above referred to were removed and a bare copper wire, No. 32, was strung out loosely on the damp ground and connected to the earth leads as in the above case. Immediately before this latter wire was put in place a mean reading was secured of the energy received, and as it was not practicable to repeat the test, a note was made of the reading of the antenna current at the sending station. When the

wire was placed upon the ground as indicated above a mean reading of the received energy was made, and the galvanometer deflection proved to be 4.7 times the value when no wire connected the stations. The ratio between the current received in each case was nearly 2.2. The hot-wire ammeter at the sending station read slightly lower at the close of the experiment than at the beginning. Reference to the above facts will be made later in the paper.

HORIZONTAL ANTENNÆ.

An antenna was next constructed by supporting a wire 14.65 m. long in a horizontal position by means of porcelain insulators fastened to stakes driven in the ground. The mean height of this

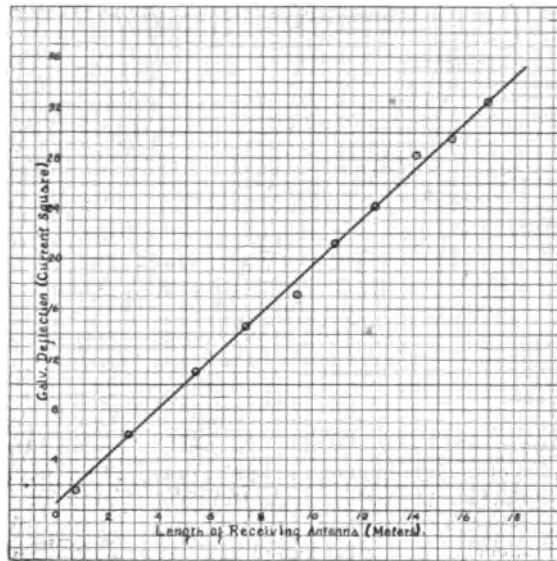


Fig. 5.

wire above the earth was .7 m. Since the receiving apparatus was located in a basement room, the permanent horizontal portion of antenna (*H*, Fig. 6) which led from the table containing the receiving apparatus to the exterior of the building was on a line with the horizontal antenna above referred to, thus making a total length of 16.8 m. Since it has been shown by Marconi, Fleming and others that such a horizontal antenna is most efficient when its free

end is pointing directly away from the sending station, the above wire was placed in this position, the direction being determined first approximately by experiment and afterwards by means of a theodolite.

After the system thus established was brought into resonance with the sending station, which in this case was grounded to gas piping, the receiving station being connected to the earth plate, readings of the galvanometer deflections were taken as various portions of the horizontal receiving antenna were cut off. After any portion of the antenna was removed the system was again tuned to resonance. Table II. gives the result of this experiment. In Fig. 5 galvanometer deflections are plotted against length of receiving antenna. Though some of these points do not lie exactly on the curve, yet other data taken confirms the fact that *in the case of a horizontal antenna under the conditions with which we worked the square of the current received is proportional to the length of the antenna.*

TABLE II.

Shunted Capacity Necessary to Effect Resonance.	Length of Horizontal Receiving Antenna.	Gal. Deflection.	Shunted Capacity Necessary to Effect Resonance.	Length of Horizontal Receiving Antenna.	Gal. Deflection.
0.001559 m-f.	16.80 meters.	32.5	0.001600 m-f.	9.40 meters.	17.2
0.001571 "	15.50 "	29.5	0.001609 "	7.40 "	14.7
0.001581 "	14.20 "	28.2	0.001613 "	5.40 "	11.0
0.001591 "	12.50 "	24.2	0.001615 "	2.75 "	6.0
0.001593 "	10.90 "	21.2	0.001617 "	0.65 "	1.6

EFFECT OF ORIENTATION ON VARIOUS FORMS OF ANTENNÆ.

Capacity-areas.—To test the effects of orientation on different forms of antenna several types were constructed and tested. The first form experimented with consisted of a capacity-area 1 m. square made by tacking a piece of sheet tin to a wooden frame and supporting this by means of a metal rod passing through porcelain insulators attached to the supporting frame-work. The rod serving as an axis was supported by a wooden tripod. 1.05 m. of wire, nearly horizontal, connected this capacity-area to the permanent antenna lead (*H*, Fig. 6), the wire being soldered to the middle of the bottom edge of the tin. This capacity-area was supported at a

height of 70 cm. above the ground at the point where the tripod stood and at a height of 16 cm. above the mean level of the ground between the two stations. By thus placing the area close to the ground it was possible to eliminate any effect due to any vertical wire leading to the same. Fig. 6 shows the general arrangement of parts in this and several succeeding experiments. The arrange-

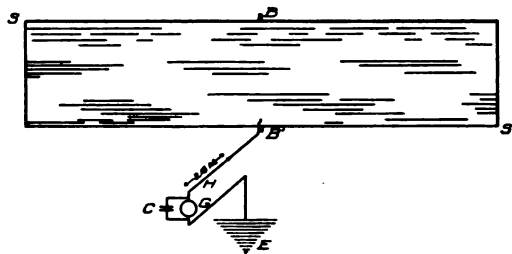


Fig. 6.

ment indicated permitted of rotating the capacity-area about a vertical axis. After bringing the system into resonance with the sending station, it was found that *the amount of energy received was the same for all planes of orientation about a vertical axis.*

The same area was next arranged in such a manner that orientation about a horizontal axis was possible. Other conditions were the same as in the previous case except that the area was supported 25 cm. above the mean level of the ground, and a vertical wire 75 cm. in length connected the middle of the tin sheet to the short horizontal lead *H* before mentioned.

Readings of the energy received were made for various angles as the capacity-area was rotated about its horizontal axis. The mean of a number of readings showed that the area when in a vertical position produced a galvanometer deflection 5.6 per cent. (current 2.7 per cent.) greater than when horizontal. The difference between the maximum and minimum values is so small that it was not deemed of value to insert readings for intermediate angles.

Since the above results obtained on rotating the capacity-area about a vertical axis do not agree with the results obtained by Dr. De Forest,¹ it was decided to test the matter further. Accordingly

¹ "With a mechanism of this character having a collecting-screen 6×15 feet in size, I have been able to locate with certainty a transmitting-station seven miles distant within

a "collecting-screen" $4.17 \times .71$ m. was made of tin plates soldered together and fastened to suitable frame-work. The general arrangement of support was the same as for the smaller area (see Fig. 6), the center of the screen being 90 cm. above the earth at the point of support. A wire nearly horizontal, 2.67 m. in length, connected the middle of the lower edge of the metal surface to the lead, *H*. The screen was free to rotate about a vertical axis at its middle point.

After resonance was effected readings of energy received were made for various angles of rotation. *In this case a difference of 4.6 per cent. in the galvanometer deflection (current 2.4 per cent.) was found to exist, the greater amount of energy being received when the collecting-screen was broadside on to the waves.* Intermediate values are not recorded here. The above difference is by no means as great as that recorded by the investigator above referred to. It is to be remembered however that Dr. De Forest used the relative loudness of sounds in a telephone receiver as judged by the human ear as a means of determining the amount of energy received for various positions of his collecting-screens. It can scarcely be said that such equipment permitted of accurate quantitative measurements. Nevertheless it is possible that the same law does not obtain for both short and long distances.

HELIX.

To test the effects of orientation upon an open circuited coil of large diameter when utilized as a receiving system a helix was constructed by winding two complete turns of wire about a wooden frame 1.5 m. square. This helix had an inductance of .040982 milli-henrys (Fleming-Anderson method). The helix thus made was supported and insulated as in the case of the small capacity-area, the free ends of the wire being at the middle of the lower edge of the coil. 1.7 m. of wire connected one end of the helix to the lead, *H*. The helix was so arranged as to permit of rotation about a central vertical axis. When resonance was secured in the usual manner energy readings were noted for various planes of orientation.

10 degrees, the transmitting-station being one designed for signal-transmitting purposes." U. S. Patent No. 771,818, October 11, 1904, line 94.

It was found that such an open circuited helix collected an equal amount of energy in all positions.

The experiment was next tried of breaking the ground connection at the receiving station and in its place making a connection to the remaining free end of the helix above described, thus making a closed oscillating system without earth connections. In the case last outlined the galvanometer showed a deflection of 87.5 mm. With the closed helix just described placed tangential to the wave front the deflection was only 5 mm., and when the helix was turned through 90 degrees so as to have its plane normal to the wave-front the deflection was so small as to be scarcely readable. *The energy received by a closed helix apparently does not follow the same law as that of the open coil.* These results are somewhat surprising for if we assume the presence of a free Hertzian wave we would expect the open circuited helix to show a difference on orientation as well as the closed circuited coil.

SCREENED VERTICAL ANTENNA.

The foregoing experiments gave rise in the mind of the writer to the thought that possibly the greater portion, if not all, of the energy transmitted in wireless telegraph operations is propagated by means of electric oscillations *through the surface of the earth and not by means of the free ether surrounding the same.*

With this thought in mind the following experiment was devised. Two vertical antennæ each consisting of a single wire 6.2 m. in length were erected 17 cm. apart, and were so arranged at the base that either could be quickly coupled to the lead, *H*. One of these vertical antennæ was then shielded from the free Hertzian waves by placing about it a metal cylinder made of tin, the cylinder being 10 cm. in diameter and 6.2 m. long. The enclosed wire hung freely within the metal tube which was insulated from the earth. Resonance was separately effected for both open and enclosed antennæ. On two different occasions several series of readings were taken in alternate groups, the results for the two tests agreeing within less than .1 of 1 per cent. The shielded antenna produced a mean galvanometer deflection 9.3 per cent. less than the unscreened system. This is equivalent to a difference of 4.9 per cent. in the value of the

current in the two cases. The results of this experiment will be discussed elsewhere.

RELATIVE EFFICIENCY OF VARIOUS ENERGY-COLLECTING SYSTEMS.

We were now in a position to carry out a series of experiments designed to determine the relative efficiency as energy-gathering devices of the several types of antennæ now in commercial use. One or two original systems were also devised and tested. The two vertical single-wire antennæ described in the last experiment were so arranged as to permit of being connected at both the top and bottom, thus four different modifications of one system were possible. The metal cylinder used to enclose the vertical antenna of the last experiment was also suitably arranged to be used as a receiving system. The several cases are illustrated diagrammatically in Fig. 7 and will be referred to hereafter as systems *A*, *B*, *C*, *D* and *E*, as indicated in the drawing.

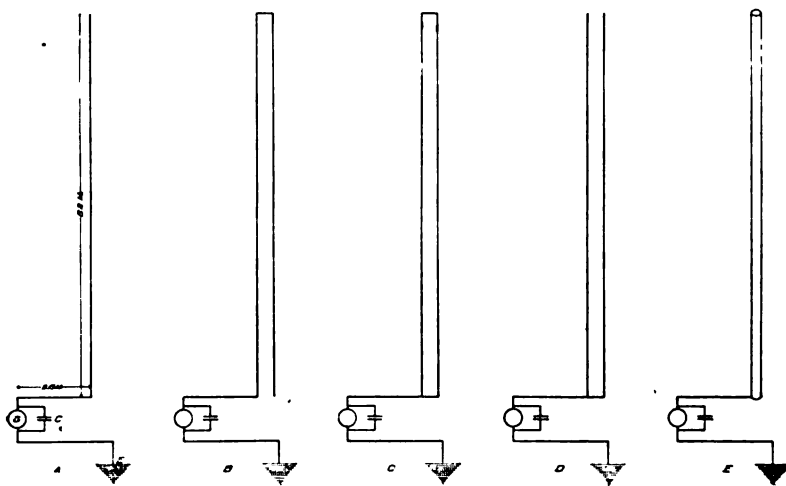


Fig. 7.

After the capacity¹ of the vertical portions of these systems was measured the systems were each in turn compared as energy-gathering devices with the simple vertical wire, *A*, taken as a standard. In these tests the readings for any given comparison were made by

¹ These and all other antenna capacity values were measured by the resonance-substitution method suggested in the paragraph on wave-length measurements.

taking several alternate groups of observations consisting of three or five readings each, thus eliminating the effects from any possible change at the sending station. (This method of taking readings was followed in all experiments constituting this investigation unless otherwise specified.) The mean ratios of the galvanometer deflection due to the energy received are to be seen in Table III., as are also the ratios of the current values in each case.

TABLE III.

System.	Capacity in Microfarads.	Ratio of Gal. Deflections Produced by Various Systems to that Caused by Standard System A.	Ratio of Current Values. (Sq. Root of Gal. Deflection.)
<i>A</i>	0.000032	1.000	1.000
<i>B</i>	0.000056	2.220	1.488
<i>C</i>	0.000068	2.045	1.450
<i>D</i>	0.000080	2.225	1.490
<i>E</i>	0.000060	3.520	1.880

It is apparent from an examination of Table III., that systems, *B* and *D*, are of practically equal efficiency. *C*, though very close to both *B* and *D* in value, showed a persistently lower efficiency. The difference is, however, only slight. It would appear that in erecting multiple-wired antennæ it is practically immaterial whether the component parts are connected at the lower, upper or both ends. Though the metal cylinder shows an apparently greater efficiency than the double-wire type, yet when other obvious factors are considered it is doubtful if such a system possesses any material advantage over the multiple-wire arrangement. The results would also seem to indicate that capacity is not as important a factor in determining the amount of energy received by a given system as is commonly supposed.

In the concluding series of experiments the relative efficiency of several systems already described, together with one or two original arrangements, were tested. The standard of comparison being a single vertical antenna 9.8 m. in length. The systems investigated in these tests were: a large capacity-area $4.2 \times .7$ m.; a small capacity-area; a large helix, 1.5 m. square, having 12 m. length of wire; a small helix, 15 cm. square, having 12 m. length of wire; a horizontal antenna, 9.8 m. in length; a wire screen, 1

m. square; a special system. The capacity-area, large helix and horizontal antenna were those used in previous experiments. The small helix was made by winding 11.1 m. of wire in 11 turns on a wooden frame $15 \times 15 \times 11$ cm., .9 m. serving as a vertical lead to connect with the horizontal lead at the top of the supporting tripod. The small helix was so arranged that its center was at the same height above the ground as that of the larger helix. The inductance of the smaller coil was .056 milli-henrys. The wire screen consisted of a piece of wire netting, 1 m. square and having a mesh .5 cm. square, fastened to a wooden frame. As in the case of the small capacity-area a vertical wire .75 cm. long connected the middle of the screen to the horizontal lead. The special system consisted of 9.8 m. of wire fastened to a light wooden rectangular frame, in the manner indicated in Fig. 8.

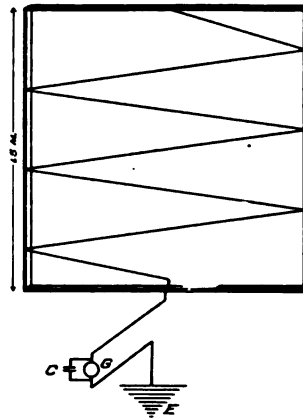


Fig. 8.

In all cases the systems were carefully insulated from the supporting structures by means of porcelain insulators. As in the tests on orientation, the large capacity and large helix were supported 70 cm. above the surface of the earth at the point of erection, and 16 cm. above the mean level between the two stations. The special system was supported in the same manner. The small capacity-area and the screen were 80 cm. and 25 cm. respectively above the surface and mean level. In the two last mentioned systems 1.5 m. of wire, nearly horizontal, led from the top of the supporting tripod to the lead, H . In the case of the large and small helices and large capacity this connecting wire was 1.7 m. long. Readings were taken in the manner described in the previous experiment. The results are recorded in the following table.

An examination of the above table shows that *all of the receiving systems tested fell far short in efficiency in the matter of intercepting energy when compared with a single vertical wire.* The nearest approach to the vertical wire in the matter of efficiency is made by

TABLE IV.

System.	Inductance in Milli-henrys.	Capacity in Micro-farads.	Ratio of Gal. Def. Produced by Various Systems to that Caused by Standard.	Ratio of Current Values.
Standard vertical antenna.		0.000049	1.0000	1.0000
Large capacity-area.		0.000106	0.4060	0.6360-
Small capacity-area.		0.000008 (?)	0.1750	0.4190
Large helix.	0.041	0.000044	0.2520	0.5020
Small helix.	0.056	0.000034	0.1060	0.3260
Horizontal antenna.		0.000340	0.1730	0.4160
Wire screen.		0.000044	0.1970	0.4440
Special system.		0.000030	0.2290	0.4790

the large capacity-area which has an efficiency in current value of a trifle over 63 per cent. It is to be noted, however, that this system has a capacity of more than twice the value of that of the standard antenna. This fact bears out the statement previously made in reference to the effect of capacity in a receiving system. It may also be observed that the horizontal antenna, at least when placed comparatively near the earth, has a relatively small efficiency. The small capacity-area, though only 1 m. square, shows a slightly greater efficiency than the horizontal system, and the wire screen is even still more efficient relatively. The case of the large and small helixes is also of interest. The smaller coil, though having the same length of wire as the larger shows a material falling off in energy received when compared with the larger. This difference may possibly be due to the greater impedance of the smaller helix. When comparing both large and small helixes with the standard type, it is to be remembered that these coils were each made up of 12 m. of wire, while the single wire standard consisted of only 9.8 m. From a practical point of view when length of wire, facility of erection and ease of maintenance are considered the special type shows the greatest efficiency as a receiving system. Its efficiency would probably have been materially increased had its lengths of wire been made to run vertical instead of nearly horizontal.

The resonance curve shown in Fig. 9 above is inserted to show the general properties of the two waves sent out by the sending station. The data for this curve was taken when using the capacity-

area 1 m. square as a receiving system. Capacity shunted about the galvanometer is plotted against galvanometer deflections. The lesser maximum probably corresponds to the shorter of the two wave-lengths radiated by the transmitting station and the greater

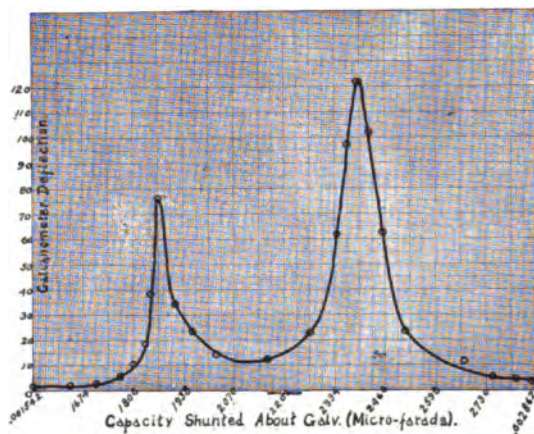


Fig. 9.

maximum to the longer wave-length. However, this relation is somewhat difficult to determine, because of the fact that these maxima would frequently interchange places. The reason for this rather unusual phenomenon we have as yet been unable to determine.

RESULTS.

To recapitulate, the foregoing data would indicate, under the conditions which obtained in these experiments: (1) that the resistance of the earth between the two stations is an important factor in the propagation of energy; (2) that the square of the energy received by a horizontal antenna is approximately proportional to its length; (3) that relatively small capacity-areas show equal efficiency in all planes of orientation about a vertical axis; (4) that even in the case of capacity-areas whose length is great compared with the width only a slight decrease in efficiency is noticeable when the area is normal to the wave front; (5) that open-circuited helixes are equally efficient in all planes of orientation; (6) that the energy received by such a helix having a given length of wire is a function

of its dimensions ; (7) that an aerial almost completely screened is but slightly less efficient than a similar unscreened system ; (8) that in dealing with multiple-wired antennæ it is practically immaterial as to whether the component parts are connected at the lower, upper or both ends ; (9) that in considering different types of receiving systems the actual capacity is not so important as is the manner in which this capacity is distributed ; (10) that of the types tested the system consisting of one or more wires normal to the earth's surface is by far the most efficient ; (11) that the energy is propagated through the surface of the earth and not by means of a free ether wave.

DISCUSSION.

The comparative closeness of our stations afforded us a special opportunity to study the effects due to the free Hertzian waves as differentiated from the effects due to the propagation of energy in other possible ways. Stone¹ maintains that the greater portion of the energy transmitted resides in that part of the wave which is immediately adjacent to the surface of the earth. It will be remembered in this connection that our capacity-areas were placed very close to the surface of the earth. If the free wave ever enters as an important factor it should, according to the commonly accepted view, have produced marked effects in our experiments, but, on the contrary, we find in the cases where the capacity-areas, helixes, etc., were rotated about a horizontal axis variation in the plane of orientation produced but slight changes in the amount of energy received, and in some instances resulted in no change whatever. The complete screening of the vertical antenna reduced the received energy but a small per cent. and even this change may have been due to causes other than the shielding effects due to the metal enclosure.

In the experiments having to do with earth resistances the increase in the quantity of energy received was probably not wholly due to the decrease in the resistance between the two stations, but it is reasonable to suppose that the greater part of the increase may be ascribed to this cause.

In view of the facts just enumerated, and since a fixed wavelength and constant supply of energy was radiated from the trans-

¹Stone, Transactions International Electrical Congress, St. Louis, 1904, p. 558.

mitting station, it would seem that the conclusion is not wholly unwarranted that practically all the energy taking part in wireless telegraph operations is propagated through the surface of the earth by means of electrical oscillations and not by means of free Hertzian waves.

The experience of those engaged in practical wireless work bears out the conclusion of the author in this respect. It is well known that when working over land a slight fall of rain on dry soil materially increases the signalling distance. The fact that it is possible to signal through greater distances over sea than over land we believe to be due to the greater conductivity of the water. The originator of one of the wireless systems now in commercial use informs the writer that in some recent tests made it was found that when operating overland the presence of iron bearing ore in the earth materially increased the signalling distance. Neither the author's experience nor the instance just cited bear out the contention of Sacks¹ who maintains that any good conductor in, or in connection with, the earth is detrimental in its effects. Kimura² also holds that the earth resistance does not figure as a factor but that the capacity of the earth plate is the important consideration. The above commercial and theoretical experiments do not tend to confirm this view.

Again, if the theory of a free ether wave is correct, the law of inverse squares should hold, approximately at least. That this law *does not hold* has been shown by several investigators among whom may be mentioned Duddell and Taylor,³ who found that the product of the distance by the intensity was a constant, and Chant,⁴ who also found that the energy fell off inversely as the simple distance.

In considering the possible processes by which energy is propagated in wireless telegraphy it is to be remembered that the beginning of wireless telegraphy as a practical commercial project dates from the time when Marconi first *connected his transmitting apparatus to earth*. The distances over which communication was effected prior to this were insignificant. In fact, until that time the transmission

¹ J. S. Sacks, *Ann. der Physik*, Vol. 18, p. 348.

² Kimura, *Phys. Zeitcher*, June 29, 1901.

³ *Institute Electrical Engineers Journal*, Vol. 35, p. 321.

⁴ *American Journal of Science*, Vol. 18, p. 403.

of intelligence by means of electric waves was little more than an interesting laboratory experiment. In a paper read before the International Electrical Congress, which convened at St. Louis, 1904, Count Solari made the following significant statement: "In other words he (Marconi) made the great discovery that two rods of metal placed *upright in the ground* at some distance apart *form a gigantic and novel oscillator in which electric oscillations set up in the one part are propagated through the earth to the other part*,¹ and at the same time electrical waves formed by the alternations of electric strain directed perpendicularly to the earth and the associated magnetic forces parallel to the earth, are propagated through the ether between the two vertical wires." We hold that the first factor mentioned by the authority just quoted constitutes the vital consideration, and that it was due to this principle that Marconi succeeded in making long distance transmission possible. We do not dispute the existence of the free ether wave but maintain that its effect is nill beyond comparatively short distances from the radiating system.

May we not think of a wireless transmitting apparatus when in operation as impressing upon the earth, at the point where the system is grounded, a high frequency alternating potential, these waves of potential spreading out through the surface of the earth in all directions? If we suppose such a process as taking place, another conductor placed in a vertical position at a distant point and connected either directly or inductively with the surface of the earth would be charged to the oscillating potential represented by the electric earth-wave at that point. Thus we would have the energy transmitted to the receiving system. The resistance of the earth would doubtless diminish the amplitude of the potential wave, hence the importance of high earth conductivity between two stations. It is more than probable that such a potential wave is confined to a very thin stratum of the earth's surface as is maintained by Poincare.²

We are aware that at least one empirical fact is difficult of explanation on the basis of the theory which we advance. Professor Fleming quotes the observations of Captain Jackson, of the

¹ The italics are ours.

² H. Poincare, Bureau des Long. Ann., 1902.

British Navy, relative to the effect of intervening land upon signalling distance, the observation being that hilly or stony ground intervening between two stations greatly decreases the amount of energy transmitted, thus reducing the signalling distance. Lieutenant-commander Robinson of the United States Navy informs the writer that it is a common experience in the Navy to have signals cease almost instantly when an elevated body of land comes to intervene between two vessels or a vessel and a land station. Lieutenant Robinson made the significant remark that "Every hill casts its shadow." We grant this, but we believe that the sudden decrease in energy when passing behind elevated bodies of land can be accounted for on other grounds than that of the electrical shadow in the commonly accepted sense of the term. The author is at present designing a series of experiments by which he hopes to prove this contention.

The phenomenon of the effects of light and darkness upon the propagation of energy we admit is not readily explicable on the assumptions which we advance. However a number of important facts which are difficult to account for upon the idea of a free Hertzian wave become easy of explanation on the basis of the oscillation theory, one notable example being the case of Marconi's Trans-Atlantic communication. This is difficult to explain on the basis of a free ether wave, as is cited by Poincare,¹ but presents no particular difficulty when viewed in the light of the theory outlined above. Notwithstanding the failure of the proposed theory to account for several phenomena encountered in practical wireless work, we believe such a theory accounts for more of the facts now known than the conventional idea of a free energy wave.

RANDAL MORGAN LABORATORY,
UNIVERSITY OF PENNSYLVANIA,
May 1, 1907.

¹ H. Poincare, Proc. Roy. Soc., Vol. 72, July 8, 1903.

NEW BOOKS.

Electricity Meters: Their Construction and Management. By C. H. W. Gerhardt. Pp. i + 326. London, The Electrician Printing and Publishing Company, 1906.

This book purports to be a practical manual and as such is eminently successful. Physical theory and mathematical discussion are passed by and the whole aim of the book has been to meet the needs of central station managers, engineers and students who wish full information in regard to the installation, use and maintenance of meters. Meter testing is discussed in great detail, and included with it is a complete description of meter testing equipment. The book is written primarily from a British standpoint, the author being chief of the Testing Department of the Metropolitan Electric Supply Company, London. It is the counterpart of American Meter Practice by L. C. Reed. The treatment is much more complete.

F. BEDELL.

Graphical Treatment of the Induction Motor. By ALEXANDER HEYLAND. Translated by G. H. ROWE and R. E. HELLMUND. Pp. i + 48. New York, The McGraw Publishing Company, 1906.

On account of the important place now taken by the Heyland Diagram in the study and tests of induction motors, this translation of Heyland's original work will be much appreciated. One is impressed with the simplicity and clearness of exposition with which the subject is developed. Although the subject has been amplified and more elaborately treated by recent writers, the student might very well peruse this little book before taking up more extensive treatises.

F. BEDELL.

THE PHYSICAL REVIEW.

THE INFLUENCE OF MOLECULAR STRUCTURE UPON THE INTERNAL FRICTION OF CER- TAIN ISOMERIC ETHER GASES.¹

BY FREDERICK M. PEDERSEN.

THE following investigation of the coefficients of friction of a group of isomeric ether gases, was undertaken with a view of determining whether the differences in molecular structure which are believed to exist in these isomeric compounds, are accompanied by differences in such a physical property as their internal friction.

It has been demonstrated² that the coefficient of friction of a gas

$$\eta = \frac{MG}{4\pi s^2}$$

where M is the mass of a molecule, G the mean value of the velocity as deduced from the mean kinetic energy, and s equals the distance between the center of two molecules at impact, or the diameter of the sphere of action. In isomeric compounds M is constant, and if the temperature is constant, G is also constant, so that if a difference in friction is observed, this difference must be due to a change in s , and, therefore, to a change in the size or the shape of the molecules owing to their different internal structure.

Investigations along this line were made by Meyer & Schumann,³ in 1881. They determined the coefficient of internal friction by the well known transpiration method. Their apparatus consisted

¹ A paper read before the American Physical Society, March 2, 1907.

² O. E. Meyer's Kinetic Theory of Gases, 1899, p. 179.

³ Wied. Ann., 1881, Bd. 13, p. 1.

essentially of a capillary nearly 1.5 meters in length coiled into a helix and fastened into the upper part of a boiling flask. The lower end of the capillary passed through the neck of the flask into a condenser. The substance to be examined was boiled at a regulated pressure, the vapor evolved surrounding the capillary and raising it to the same temperature. Part of the vapor which was, of course, saturated, entered the upper end of the capillary and passed through it into an air-free, cooled space where it was condensed and measured as a liquid. The volume of the vapor transpired was calculated from the amount of the liquid collected in the condenser.

Their method is open to criticism for several reasons. Objection might be made against the coiling of the capillary into a small helix because its bore may have thus been deformed and the curved path of the gas may have caused additional resistance. The vapor at the boiling point of the liquid can also hardly be regarded as a true gas, and should have been tested at several degrees above boiling. The expansion of the saturated vapor as it passed through the capillary probably also changed its state. Furthermore, the great length of time, several hours, needed for transpiration made it difficult to keep conditions constant.

TABLE V.
Esters $C_n H_{2n} O_2$ $\eta \times 10^6$.

Acid Radical.	Alcohol Radical.				
	Methyl.	Ethyl.	Propyl.	Isobutyl.	Amyl.
Formic acid.	$n = 2$	3	4	5	6
	173	156	159	172	160
	$n = 3$	4	5	6	7
Acetic acid.	152	152	160	155	
	$n = 4$	5	6	7	8
	150	158	153	164	158
Propionic acid.	$n = 5$	6	7	8	9
	159	160	164	167	155
	152	151	153	158	155
Isobutyric acid.	$n = 6$	7	8	9	10
	163	165	167	154	
Valerianic acid.					

Two capillaries were employed, one 1427 mm. long and 0.31 mm. in diameter; the other 1404 mm. long and 0.3328 mm. in diam-

eter. The second capillary gave values 3 per cent. higher than the first. Above is the table of their results for esters :

They conclude that all esters at their boiling points and at the same pressure transpire very nearly equal volumes of vapor, which, however, because the boiling points are different, do not contain the same number of molecules.

They found η for the corresponding acids considerably smaller than for their esters. They believed that the differences of η are partly too small and partly too irregular to draw any sure conclusion of the dependence of η on the molecular constitution. They point out, however, some differences which seem quite regular.

The esters of acetic, propionic and isobutyric acids show almost always a smaller η than those of formic, normal butyric and valeric acids. This difference is especially noticeable in the two butyric acids. The influence of the alcohol radical cannot be seen so clearly. Among the isomeric esters, those of formic, acetic, propionic and isobutyric acids have the greater η with the greater alcohol radical. The isomeric esters of normal butyric and valeric acids do not follow this rule but have the same friction.

The number of carbon atoms in a molecule also seems to have a certain influence on η . The esters for which $n = 2, 5, 7$ or 8 show a larger η than those with 3, 4 or 9 carbon atoms. The cause of these differences they were unable to explain.

On calculating the relative molecular volumes they found them only about half those given by Kopp's rule. L. Meyer tried to account for this by advancing the hypothesis that by Kopp's method the empty space is included which is open to the atoms for their motion, while from the coefficient of internal friction only the volume of the gas particles themselves is determined.

Steudel¹ continued the work of L. Meyer and Schumann, using the same apparatus with the second capillary, the first having been broken. He investigated several homologous lines of organic compounds, viz.: alcohols up to four atoms of carbon per molecule, and their halogen derivatives, also some substitution products of ethane and methane.

He found the transpiration time increased with the molecular

¹ Wied. Ann., 1882, Bd. 16, p. 369.

weight. Of isomeric compounds at the boiling points, the normal, *i. e.*, those that boil at the highest temperature transpire the slowest and the tertiary the fastest, with the exception of isopropyl alcohol which transpires noticeably slower than the normal. Unsymmetrical low boiling compounds have a smaller transpiration time than the symmetrical. The only exception he found to the rule that the transpiration time increases with the molecular weight is methyl iodide whose time was 1,037 minutes, which is almost the same as 1,056 minutes taken by isobutyl iodide.

He points out that the coefficients of friction of each line of homologous compounds are nearly alike or only slightly different. The values for the primary alcohols vary from .000135 to .000143; for three of them they are almost exactly alike. The isopropyl gave a considerably larger figure, also the tertiary butyl. The chlorides seem to all have the same friction. The greatest differences exist in the iodide column.

TABLE OF $\eta \times 10^6$.

Radical.	Alcohol.	Chloride.	Bromide.	Iodide.
Methyl.	135	116 ¹		245
Ethyl.	142	105 ¹	183	216
Normal propyl.	142	146	184	210
Isopropyl.	162	148	176	201
Normal butyl.	143	149		202
Isobutyl.	144	150	179	204
Tertiary butyl.	160	150		

He found a considerable difference in η with a change in pressure. With a greater pressure than 10 to 15 cm. of mercury the formula seemed to lose its validity for vapors. This agrees with what L. Meyer had noticed with benzole.

Steudel also gives tables of molecular velocities, mean free paths, combined cross-section of molecules and cross-sections of an equal number of molecules. He points out that the cross-sections of molecules of isomeric compounds are not the same. For the butyl compounds the areas for the normal substances are the largest, the tertiary the smallest, with the iso compounds between. Propyl and isopropyl alcohol, as also both chlorides show the same relation.

¹ Calculated from Graham's results.

On the other hand, isopropyl-bromide has a greater molecular area than the normal compound. In the substitution products of ethane the symmetrical ones have a larger area than the unsymmetrical.

Steudel also calculated the relative molecular volumes from SO_2 according to the method of L. Meyer, with whom he agrees in finding the volumes about one half as large as those calculated according to Kopp's rule. The ratios of molecular volumes of the different substances, however, are almost the same as the ratios of the volumes according to Kopp.

L. Meyer,¹ summing up Steudel's and his own previous results, gives the following :

TABLE OF $\eta \times 10^6$.

Alcohols	$\text{C}_n\text{H}_{2n+2}\text{O}$	142 average
Chlorides	$\text{C}_n\text{H}_{2n+1}\text{Cl}$	150 "
Esters	$\text{C}_n\text{H}_{2n}\text{O}_2$	155 "
Bromides	$\text{C}_n\text{H}_{2n+1}\text{Br}$	182 "
Iodides	$\text{C}_n\text{H}_{2n+1}\text{I}$	210 "

Cases in which $n = 1$ and some few unaccountable variations are omitted from the above. When $n = 1$ the variations are great but he could see no law of the influence of molecular constitution on the friction.

On the other hand the influence of the nature of the atom is very clearly seen ; friction of iodine > bromine > chlorine.

The molecular volumes do not agree with those of L. Meyer² calculated from Graham's results. He points out that this one fact seems certain, viz. : the molecules of a tertiary butyl compound are smaller than those of a secondary which are smaller than those of a primary. This is in agreement with the universal view taken of the concatenation of these compounds. Those of the tertiary are grouped around a single atom of carbon, hence are more spherical in shape. Propyl and isopropyl compounds on the other hand do not show the same regularity. The alcohols and iodides deviate in opposite directions, which is unexplained. He further points out that the sphere of action of a liquid molecule increases with the temperature, while that of a gaseous molecule diminishes with rise of temperature.

¹ Pogg. Ann., 1882, Vol. 16, p. 394.

² Liebig's Ann., 1867, Suppl. Bd. 5, p. 129.

METHOD EMPLOYED IN THIS INVESTIGATION.

Owing to the difficulty of getting capillaries of perfectly uniform bore, and of determining with the greatest accuracy the shape and size of their cross-section, and also owing to the possible formation of eddies at the beginning and end of the flow, and to the possible slipping of the gas on the capillary walls, probably the oscillation method is the better for absolute measurements, provided a solid body is employed of such a shape that the mathematical treatment is rigorously correct. It seems certain however that the transpiration method has been growing in favor of late years, and that it is more convenient for comparative measurements than the other method. As my object was more to get comparative than absolute values of the greatest accuracy, the transpiration method was decided upon for this experimental investigation.

GENERAL DESCRIPTION OF APPARATUS.

The form of apparatus as well as the subject of this research was kindly suggested to me by Professor Morris Loeb, then of N. Y. University, under whose guidance these experiments were made. The apparatus consists essentially of a U-shaped tube (see Fig. 1), one limb of which is capillary, while the other is not, but serves as a cylinder of known capacity, down which is forced by gravity a piston consisting of a column of mercury, which drives the gas under it up through the capillary limb. The capillary, *A*, does not begin at the bend of the U, but some distance above it. The distance between the limbs is only 3 cm., so that the apparatus can be placed inside of a glass tube 5 cm. in diameter which serves as a steam jacket (see Fig. 3), the steam being introduced through a side tube, *S*, near the top and passing out freely at the bottom, *O*. A cork, *C*, through which both limbs of the apparatus pass is on a level with the top of the capillary, and serves to close the steam jacket at the top. The mercury limb above the cork is provided with a special stop-cock, *H*, bored out to the same diameter as the tube below it. Above the stop-cock is a continuation of the tube terminating in a small funnel, *F*, for convenience in introducing ether and mercury. An ordinary thistle funnel with horizontal bottom will not answer; the bottom of the funnel must be inclined

about 45° to the axis of the mercury tube, otherwise the mercury will not so readily descend in one unbroken column when released by turning the stop-cock. Two marks, M_1 and M_2 , are etched on the mercury tube a convenient distance apart, the lower one, M_2 , being near the bend at the bottom, the volume of the tube between

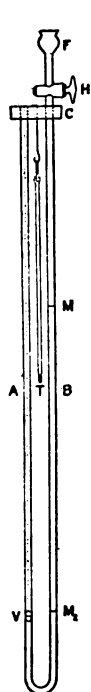


Fig. 1.
View perpendicular to the
plane of the two limbs.



Fig. 2.
View in the plane of
the limbs.

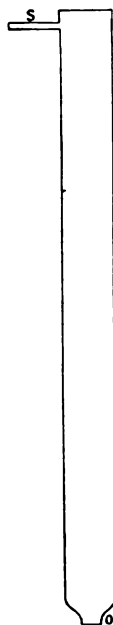


Fig. 3.
Steam Jacket.

the marks being accurately determined by calibration with mercury. The bore of this tube being slightly conical instead of truly cylindrical, its calibration was also carried far enough above the upper mark, M_1 , to cover the space passed over by the mercury column during an experiment, so that the average height of the mercury column during an experiment could be calculated.

The method of making an observation on ether gas is essentially as follows: The steam jacket being cold and filled with air the ap-

paratus is placed in it. The stop-cock is opened and about 1 c.c. of ether is poured down the mercury tube. By means of an aspirator the ether is sucked up the other limb close to the base of the capillary. The small hermetically closed tube seen at *V* in Figs. 1 and 2 serves as a reservoir for ether at the base of the capillary. Care was always taken to fill this tube completely with ether so that it could not act as an air pocket. Steam is then led into the jacket and of course vaporizes the ether, driving surplus liquid violently out through the top of the mercury tube. The stop-cock is then closed and after equilibrium has been established, a weighed amount of mercury is introduced into the funnel and allowed to flow down until it is arrested by the stop-cock, which is not quite air tight, because no grease can be used in it for fear of soiling the mercury. The stop-cock is then suddenly turned and the mercury descends in a single column. When its lower meniscus passes the upper mark on the tube a stop watch is started, which is stopped as the same meniscus passes the lower mark. The barometer is read when the mercury has covered half the measured distance. A thermometer, *T*, Fig. 1, hanging from the cork at the top of the steam jacket indicates the temperature of the steam, and serves as a plumb line. The readings of this thermometer were corrected by comparison with a standard thermometer. The coefficient of friction of the gas is calculated by the following formula given by O. E. Meyer:¹

$$\eta = \frac{\pi g d r^4}{16 L V} \frac{P^2 - p^2}{P} t,$$

in which *d* = density of mercury at 0° C.

g = acceleration due to gravitation.

r = radius of capillary in cm.

L = length of capillary in cm.

P = pressure of gas on entering the capillary.

p = height of barometer at 0° C.

t = time in seconds.

V = c.c. of gas transpired.

No allowance need be made for the expansion of the mercury at 100° C., for what the column gains in height is compensated for by

¹ Pogg. Ann., 1866, Bd. 127, p. 269.

loss in density. No allowance has been made for the expansion of the capillary as it was assumed the expansion of the mercury tube, hence increase of the volume of gas transpired, would counteract this.

The advantages of this apparatus over that devised by L. Meyer are quite obvious and numerous. In the first place it is much more simple and available. The capillary is straight instead of coiled into a helix. The friction of the vapors is taken at a temperature so high above the boiling point that they behave more like true gases than at their boiling points, where they are in a condition of unstable equilibrium. The length of time required for an experiment is short enough for all conditions to be kept constant, and yet long enough, so that with a stop watch reading to one fifth of a second, the time can be determined to within less than one part in a thousand.

APPARATUS NO. I.

The first piece of apparatus was constructed more to test the practicability of the method than for getting accurate results: It having been determined by experiment, that the largest diameter of tube in which a mercury column would hold together, against a cushion of air, was about .35 cm., this apparatus was constructed with a mercury tube whose mean diameter, where it was traversed by the mercury column was .35104 cm., as shown by the fact that 76.0405 grams of mercury occupied 58.05 cm. at 20° C. The distance between the two etched marks on the tube was 50 cm. This distance was occupied by 65.5558 grams of mercury at 20° C. The density of mercury at this temperature being 13.5463 the volume between the two marks was 4.8394 cubic centimeters.

The capillary was 34.35 cm. in length which was only about half the length of the mercury tube forming the other side of the U, in other words the capillary formed the upper half of one side of the U. Its bore was conical as shown by the fact that 9.50 cm. of mercury at the small end occupied 9.05 cm. at the larger end which was made the bottom because O. Reynolds¹ has shown that converging walls tend to a steady instead of a whirling flow of water and presumably also of gas. The above column of mercury was

¹ Proc. Royal Inst. Grt. Brit., 1884, vol. 11, p. 44.

passed slowly from one end of the capillary to the other and changed its length gradually and steadily, thus showing the absence of abnormal contractions or expansions of the bore. The bore of the capillary was determined from a sample 5.75 cm. long which had been cut from the smaller end. This sample was weighed several times empty and when containing different columns of mercury and the radius of the bore determined in the well-known way. A section was also examined under a microscope with a micrometer eye piece, and found to be so nearly a true circle that it was taken for such. The microscope reading agreed well with the mercury determinations of the radius. After taking the average of the mercury and microscope readings and after allowing for the taper of the capillary its mean radius was found to be .0103908 cm.

TABLE OF THE INTERNAL FRICTION OF AIR.

Apparatus No. 1.

Temp. in C. ^o	Ht. of Driving Col. in Cm.	Barom. at 0° C.	Press. of Entering Gas.	Time in Seconds.	$\eta \times 10^7$.	Average $\eta \times 10^7$.
15	7.97	76.03	83.09	76.04	1,872	1,863.8 $\pm$ 2.57
14.9	7.97	76.03	83.09	75.0	1,862	
14.9	7.97	76.03	83.09	74.8	1,857	
14.9	7.966	76.03	83.09	75.2	1,866	
14.9	7.966	76.60	83.64	75.2	1,860	
15.4	7.966	76.60	83.64	75.4	1,865	
20.4	4.29	75.38	78.87	156.8	1,967	1,972 $\pm$ 3.5
20.2	4.29	75.38	78.87	157.6	1,977	
21.4	9.48	75.38	84.01	64.4	1,935	1,932 $\pm$ 2.0
21.4	9.48	75.38	84.01	64.2	1,929	
99.9	9.48	75.38	84.01	75.6	2,272.5	2,296.5 $\pm$ 15.8
99.9	9.48	75.38	84.01	76.0	2,284.5	
100.3	7.98	76.96	84.00	92.0	2,238.2	
100.3	7.98	76.96	84.00	89.8	2,185.0	
100.3	7.97	76.60	83.64	94.0	2,305.0	
100.3	7.97	76.60	83.64	96.4	2,384.5	
100.3	7.97	76.60	83.64	92.7	2,293.0	
100.3	7.97	76.60	83.64	94.0	2,325.0	

To facilitate the washing of the apparatus the small vent, V , in Figs. 1 and 2, was left about $\frac{1}{2}$ cm. below the base of the capillary. This vent tube, which was only 1 cm. long, was hermetically

sealed off after the apparatus was washed and ready for use. The apparatus, after it was received from the glass-blower, was washed throughout with a solution of potassium permanganate made alkaline with caustic potash, then with a solution of the same substance made acid with dilute sulphuric acid. Later a half and half solution of potassium bichromate and strong sulphuric acid was substituted for the above. Sometimes also strong nitric acid, followed by dilute nitric acid, was used. Then followed many washings with distilled water. The apparatus was then dried, by sucking through it by means of an aspirator, hot air which was filtered through cotton and dried by calcium chloride. A column of calcium chloride was also placed in the connection between the aspirator and the apparatus. The drying was not hastened by the use of alcohol or ether. The mercury was cleansed by shaking with dilute nitric acid, passing through a fine pin hole and drying in a porcelain dish at 110° C.

The results of experiments on air with this apparatus are given in the preceding table. It will be noticed they are all rather high, but prove at any rate that the method and apparatus are practicable. The probable errors were calculated by the usual formula

$$0.6745 \sqrt{\frac{\sum \text{diff}^2}{n(n-1)}}.$$

The error for readings at 100° C. is large, probably owing to an error of the stop-watch, whose hand showed a tendency to fly forward when stopping near 90 seconds. In one case the hand flew forward 10 seconds. The watch was of course repaired as soon as this defect was noticed. A different and better stop watch was used with apparatus No. 2 and No. 3. In those cases where the mercury was allowed to run back and was used over again the readings were weighted less than independent readings, three readings being converted into two by taking their means, and four into three in the same way.

It is rather difficult to tell what is the true coefficient of the internal friction of air. Landolt and Boernstein¹ give η for air at 15° C. 1.784×10^7 . Markowski² at 16° gives 1.814×10^7 , Kleint³

¹ Phys. Chem. Tabellen, Landolt and Boernstein, 1893.

² Inaug. Diss. Halle, 1903.

³ Inaug. Diss. Halle, 1904.

at 14.1 to 14.5° C. gives $1,808 \times 10^7$. According to Landolt and Boernstein, then, my readings are $4\frac{1}{2}$ per cent. too high at 15°, while according to Markowski and Kleint they are about 3 per cent. too high. F. G. Reynolds¹ gives for air at 20.7° .000187, which is $3\frac{1}{4}$ per cent. lower than my result of .0001932 at 21.4° C.

It was found by repeated trials with di-ethyl ether that the surface tension of the mercury was so much reduced by contact with the ether gas that the mercury would not hold together in one column in apparatus No. 1. It was determined by experiment that the mercury piston could not be used for ether gas in a tube whose diameter was much larger than 2 mm. A second piece of apparatus was accordingly constructed with a mercury tube of about this size, and a finer capillary, so that the transpiration time would be increased and greater accuracy be secured.

APPARATUS NO. 2.

The capillary selected for this when examined with a simple microscope was at first thought to be circular in cross-section, but the use of a high-power microscope with micrometer eye-piece showed it to be very elliptical, the ratio of the axes being almost exactly as 3 is to 1. The area of its cross-section was determined by mercury several times, and these values averaged with the microscope reading with which they agreed well.

The capillary which was 84 cm. long tapered in its bore, 2.5 cm. of mercury at the large end becoming 2.685 cm. at the small end. The sample whose bore was determined was taken from the small end. After allowing for the taper of the bore the average semi-major axis was found to be .006057 cm. and the average semi-minor axis .002016 cm. The capillary was placed with its larger end downward and reached to within 15 cm. of the bend in the U.

The mean diameter of the mercury tube in that part traversed by the mercury piston during an experiment was .2012 cm. as shown by the fact that 31.3 grams of mercury occupied a length of 72.6 cm. at 16° C. The marks on the mercury tube were made 50 cm. apart, the volume between these marks being found by means of mercury to be 1.5707 c.c.

¹ PHYS. REV., 1904, vol. 18, p. 419; vol. 19, p. 37.

Because the capillary was elliptical the formula used for calculating the internal friction of gas from this apparatus is, according to Mathieu,¹

$$\eta = \frac{\pi d g}{8 L V} \frac{a^3 b^3}{a^2 + b^2} \frac{P^2 - p^2}{P} t$$

where a = semi-major axis of ellipse of capillary.

b = semi-minor axis of ellipse of capillary.

d = density of mercury at 0° C..

g = acceleration due to gravitation.

L = length of capillary.

V = vol. of gas transpired.

P = pressure of entering gas.

p = pressure of leaving gas = barom. at 0° C.

t = time in seconds.

The results with air with this apparatus are shown in the next table.

It will be noticed that the values of η are somewhat lower than for apparatus No. 1, and therefore nearer the correct values.

The different lengths of the capillary given in the first column are due to the fact that on several occasions the upper end of the capillary became stopped with dust from the atmosphere and had to be cut off. When not in use the capillaries were kept capped with rubber, the funnels filled with cotton and closed by corks in which were inserted tubes of chloride of calcium.

TABLE OF THE INTERNAL FRICTION OF AIR.

Apparatus No. 2.

Length of Cap.	Temp. in C.°.	Ht. of Driving Col.	Barom. at 0° C.	Press. of Entering Gas.	Time in Seconds.	$\eta \times 10^7$.	Average $\eta \times 10^7$.
81.8	12.5	23.17	75.74	97.92	2,604	1,864.2	1,897.3 ± 3.5
84	18.5	23.17	76.19	98.36	2,721	1,897.4	
84	19.9	23.15	76.26	98.41	2,715	1,892.0	
84	19.9	23.42	76.41	98.82	2,700	1,902.5	
84	20.9	23.15	76.26	98.41	2,730	1,902.2	
84	26.9	23.16	76.15	98.31	2,810	1,957.1	
84	29.1	23.17	75.90	98.08	2,830	1,973.6	
84	100	23.17	75.91	98.09	3,201	2,233.0	2,242 ± 5
81.8	99.9	23.14	75.70	98.85	3,130	2,237.0	
81.8	100.2	23.14	76.51	98.65	3,155	2,257.0	

¹ Compt. Rend., 1863, Tome 57, p. 320.

Apparatus No. 3.

73.25	10	18.746	76.78	94.56	509.8	1,843.8	
73.25	13.3	18.75	76.78	94.56	516	1,866.9	
73.25	14.4	18.74	76.80	94.58	518.2	1,870.0	
73.25	19.4	18.75	76.00	93.79	524.6	1,894.0	
73.25	20.8	18.74	75.99	93.78	531.2	1,917.2	
70	21.0	18.75	76.99	94.77	509.2	1,923.6	1,909.9 $\pm$ 7.2
70	20.8	18.75	76.95	94.74	500.0	1,889.0	
70	100	18.74	75.76	94.50	592.8	2,244.0	
70	100.1	18.74	76.19	94.93	599	2,267.0	2,246.3 $\pm$ 7.2
70	100.3	18.75	77.13	94.92	588.8	2,228.0	

PREPARATION OF ETHERS.

The di-ethyl ether used in the following experiments was sulphuric ether, U. S. P. purified by two washings with concentrated sulphuric acid, C. P., each of these washings being followed by one with distilled water. It was then shaken with mercury and dried with sodium wire from which it was distilled into glass tubes which were afterward hermetically sealed. The ethyl-propyl ether, methyl-propyl-ether and methyl-ethyl ether used in this investigation were prepared by me, in the research laboratory of New York University under the personal supervision of Professor Loeb, according to the continuous etherification method described by Norton and Prescott in the *Am. Chem. Journal*, 1884, Vol. VI., p. 241. They were carefully dried with sodium and kept in sealed tubes.

The other substances, viz.: di-methyl ether, ethyl alcohol, methyl-isopropyl ether, ethyl-isopropyl ether, di-propyl ether, isopropyl-propyl ether and di-isopropyl, I owe entirely to the great courtesy of Professor Loeb, as I had no part at all in their preparation. As far as is known this is the first time that methyl-isopropyl ether has ever been made, while ethyl-isopropyl ether and isopropyl-propyl ether have probably been made only once before.

The internal frictions of the ethers used in apparatus No. 2 are given in the foregoing table on page 239.

The ethers are arranged in this table in the order of their molecular weights; that of methyl-ethyl ether being 60.064, that of methyl-propyl, methyl-isopropyl, di-ethyl ether being alike 74.08; while that of ethyl propyl is 88.096. It will be noticed the smaller the molecular weight the greater is the internal friction, which

TABLE OF INTERNAL FRICTION OF ETHER GASES.

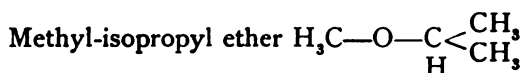
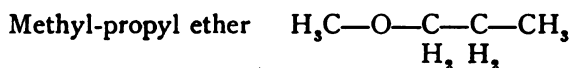
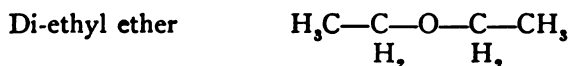
Apparatus No. 2.

Length Capillary.	Kind of Gas.	Temp. of Gas.	Ht. of Driving Col. at ° C.	Barom. at ° C.	Press. of Entering Gas.	Time in Seconds.	$\eta \times 10^7$.	Average $\eta \times 10^7$.
81.8	Methyl-	99.9	23.16	75.68	97.85	1,502.0	1,074.5	1,092.3 $\pm$ 6.4
81.8	Ethyl	100	23.20	76.09	98.30	1,537.8	1,103	
81.8	Ether.	99.9	23.19	75.87	98.07	1,471.0	1,053.9	
81.8		99.3	23.16	75.44	97.61	1,558.0	1,114.2	
81.8		100	23.06	76.28	98.35	1,550.2	1,105.4	
81.8		100	23.16	76.15	98.32	1,540.0	1,102.8	
84	Methyl-	100	23.90	76.28	99.18	1,380.0	990.9	1,004.3 $\pm$ 5.5
84	Propyl	100	23.22	76.23	98.46	1,409.6	985.4	
84	Ether.	100	23.28	76.18	98.47	1,402.2	982.5	
84		100.1	23.14	76.46	98.60	1,461.8	1,018.9	
82.5		99.9	23.13	75.31	97.46	1,440.4	1,021.2	
81.8		99.8	23.11	74.24	96.39	1,439.9	1,027.0	
81.8	Methyl-	100.3	23.15	77.15	99.30	1,481.4	1,061.1	1,054.8 $\pm$ 5.0
81.8	Isopropyl	100.3	23.14	77.10	99.24	1,526.0	1,081.1	
81.8	Ether.	100	23.13	76.01	98.24	1,459.6	1,047.3	
81.8		100	23.12	76.00	98.13	1,455.0	1,039.9	
81.8		100	23.14	76.00	98.15	1,460.8	1,044.9	
84	Di-Ethyl	100.1	23.42	76.39	98.81	1,410.0	993.4	999 $\pm$ 3.3
84	Ether.	100	23.42	76.08	98.51	1,404.0	990.6	
84		100	23.16	76.15	98.32	1,416.6	986.8	
84		100	23.17	76.10	98.28	1,417.6	988.6	
84		100.1	23.16	76.54	98.71	1,437.6	1,000.6	
82.5		99.9	23.16	75.71	97.89	1,434.6	1,017.8	
82.2		99.9	23.21	75.50	97.73	1,428.0	1,015.2	915.2 $\pm$ 5.3
84	Ethyl-	100	23.17	76.06	98.24	1,285.0	896.2	
84	Propyl	100	23.17	75.89	98.07	1,296.4	904.6	
84	Ether.	99.9	23.16	75.70	97.87	1,281.2	892.7	
81.5		99.9	23.15	75.58	97.75	1,295.8	930.5	
81.5		99.9	23.14	75.57	97.73	1,298.8	932.3	
81.5		99.9	23.15	75.57	97.74	1,300.8	934.0	

agrees well with the kinetic theory of gases, according to which the friction increases with diminished size of molecule.

The most noteworthy fact shown in this table is that the three isomeric ethers, di-ethyl, methyl-propyl and methyl-isopropyl have not the same internal friction. Di-ethyl ether and methyl-propyl practically agree, while methyl-isopropyl ether has a friction 5 per cent. higher. According to the generally accepted view of the

concatenation of the molecules of these substances, the first two are simple chain compounds, while the last is a chain compound with two branches :



It is easily conceivable how the last arrangement results in a compacter, smaller molecule, and hence shows a higher internal friction.

Although the amount of liquid used varied from $\frac{1}{2}$ c.c. to 1 c.c. as a rule, this small amount seemed sufficient on vaporizing to drive all the air out of the apparatus, as filling the apparatus entirely with ether from the base of the capillary to the stop-cock did not give results different from those obtained using 1 c.c. of ether.

The weight of mercury used in apparatus No. 1 and No. 2 was usually about 10 grams. That in apparatus No. 3 shortly to be described was about 5 grams.

The allowance to be made for the friction of the mercury against the walls of the tube was determined in the following manner. Three readings with air were taken with three very different columns of mercury, under constant temperature conditions. It being known that the internal friction of a gas is independent of the pressure, the values of η from these three readings were equated to each other in pairs, giving, after cancelling out constants of the apparatus, equations of the form

$$\frac{P^2c^2 - p^2}{Pc} t = \frac{P_1^2c^2 - p_1^2}{P_1c} t_1$$

in which c is a constant reduction factor due to the friction of the mercury against the walls of the tube. The effect of capillarity is probably negligible, because the upper and lower surfaces of the mercury are convex in opposite directions.

In solving the equations for c good agreement was found, the

average c for apparatus No. 1 being .9892. For apparatus No. 2 $c = .9895$ and for apparatus No. 3 $c = .9894$, all at 100° C. The pressure of the gas on entering the capillary was calculated by adding the height of the mercury column at 0° C. to the barometer at 0° C. and multiplying by the reduction factor given above. The mercury and barometer column were reduced to 0° C. by the aid of a table given on page 248 of Kohlrausch's *Kleiner Leitfaden der Praktischen Physik*.

APPARATUS No. 3.

In order to have a second piece of apparatus available for experiments with ether, so that two experiments could be made at the same time, a third piece of apparatus was constructed. The mercury tube of this apparatus was made a little smaller than that of apparatus No. 2, as some difficulty had been met in the mercury column failing to hold together properly. The capillary of this apparatus was also elliptical and slightly conical. The average semi-major axis as determined by the microscope and mercury was .006176 cm. while the minor axis was .002837. The length of the capillary was 73.25 cm. at first, but was reduced to 70 cm. when the apparatus was repaired after a breakage.

The distance between the marks on the mercury tube was 38.45 cm. and the volume of gas transpired was .742 c.c. since 10.0634 grams of mercury occupied the distance between the marks at 16° C. The average diameter of the mercury tube where the mercury traversed it during an experiment was .158112 cm.

A table of the results obtained with this apparatus for air is given on page 238 underneath those for air with apparatus No. 2. It will be noticed that the two pieces of apparatus agree very closely in results.

The results obtained for ethers with this apparatus are given in the following table. The first point worthy of note is that ethyl alcohol which is metameric with di-methyl ether has about three per cent. lower coefficient of friction, showing it to have the larger molecule.

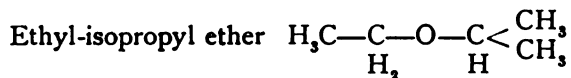
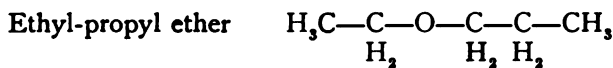
The values for di-ethyl ether, and ethyl-propyl ether agree well with those given on page 239 by apparatus No. 2.

Ethyl-isopropyl ether has a friction 4.6 per cent. higher than that of ethyl-propyl ether, hence a smaller molecule.

TABLE OF INTERNAL FRICTION OF ETHER GASES.

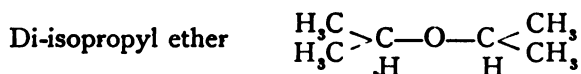
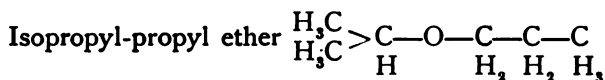
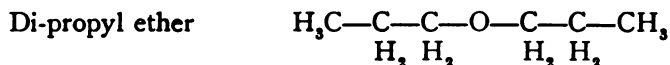
Apparatus No. 3.

Length Capillary.	Kind of Gas.	Temp. of Gas.	Ht. of Driving Col. at ° C.	Barom. at ° C.	Press. of Entering Gas.	Time in Seconds.	$\eta \times 10^6$.	Average $\eta \times 10^6$.
70	Di-methyl	100.3	18.75	77.24	95.03	315.6	1,191.8	
70	Ether.	100.3	18.74	77.32	95.10	314.8	1,188.6	1,190.2 $\pm$ 1
70	Ethyl	100.3	18.74	76.98	94.67	303.6	1,145.6	
70	Alcohol.	100.3	18.76	76.99	94.70	308.4	1,164.4	1,155 $\pm$ 6.3
73.25	Di-ethyl	100.1	18.78	76.43	94.26	287.4	1,041.8	
73.25	Ether.	100	18.60	76.15	93.81	287.4	1,023.2	
73.25		100	18.79	76.03	93.88	270.4	978.4	1,001 $\pm$ 8.15
70		99.9	18.76	75.80	93.61	254.8	963.7	
70		100.1	18.56	76.46	94.07	266.5	998.1	
73.25	Ethyl-	99.9	18.76	75.79	93.61	253.2	914.8	
73.25	Propyl	99.9	18.26	75.74	93.06	267.2	939.3	
73.25	Ether.	100	18.05	76.39	93.50	262.4	921.7	918.4 $\pm$ 4.2
73.25		100.3	18.28	76.83	94.16	256.6	902.7	
73.25		100.4	18.05	77.02	94.14	263.2	913.7	
70	Ethyl	100.2	17.74	76.46	93.26	267.7	946.4	
70	Isopropyl	100.2	18.76	76.41	94.22	255.4	966.4	960.7 $\pm$ 5
70	Ether.	100.2	18.56	76.34	93.95	258.8	969.3	
70	Di-Propyl	100	18.75	75.95	93.73	222.2	839.5	
70	Ether.	100	18.76	76.02	93.74	222.0	839.3	837.5 $\pm$ 1.26
70		100.3	18.75	77.14	94.93	220.8	832.7	
70	Isopropyl-	100.1	18.73	76.19	93.97	230.4	870.2	873.4 $\pm$ 2.2
70	propyl	100.1	18.76	76.22	94.03	231.6	876.6	
	Ether.							
70	Di-isopro-	100.3	18.74	77.14	94.92	230.2	869.2	
70	pyl	100.3	18.74	77.14	94.92	230.8	871.5	
70	Ether.	100.3	18.76	77.09	94.89	239.0	902.8	894.3 $\pm$ 5.95
70		100.3	18.74	77.13	94.91	236.0	890.7	
70		100.1	18.73	76.23	94.01	241.0	910.5	
70		100.1	18.75	76.23	94.03	243.6	921.2	



Isopropyl-propyl ether has a friction 4.3 per cent. higher than that of di-propyl ether, while di-isopropyl ether has a friction 6.8

per cent. higher than di-propyl. This is in accordance with our view of the concatenation of the atoms in these molecules. Di-propyl ether is a straight, chain compound whereas isopropyl-propyl has two branches and di-isopropyl has four branches.



As already noticed the difference between methyl-propyl and methyl-isopropyl is 5 per cent. due to two branches; the difference between ethyl-propyl and ethyl-isopropyl due to two branches is 4.6 per cent.; the difference between di-propyl and isopropyl-propyl is 4.3 per cent. due to the same number of branches. The diminishing effect of the two CH_3 branches is probably due to the fact that the molecules of the substances lower on the lists are larger, hence the branches have a smaller relative effect. It would seem that di-isopropyl ether ought to be 8.6 per cent. higher than di-propyl whereas it is only 6.8 per cent. This discrepancy I am unable to explain.

Di-methyl ether, being a gas at ordinary temperatures, had to be handled differently from the other ethers, all of which were put into the apparatus as liquids. The low boiling ethers, methyl-ethyl, and methyl-isopropyl were experimented upon in a room whose temperature was at or very near 0°C .

The di-methyl ether gas was kept in sealed glass bulbs of 250 c.c. capacity. The lower end of a bulb was connected by rubber tubing to a reservoir of mercury while the upper end was connected by a rubber tube to the funnel at the top of the apparatus. After the aspirator had created a partial vacuum in the apparatus by sucking the air out through the capillary, the tips of the bulb were broken off inside the rubber tubes and mercury allowed to flow into the bulb gradually from the bottom, driving the ether gas before it into the apparatus, the action being assisted all the while by the suction

of the aspirator. As 250 c.c. was many times the cubic capacity of the apparatus, by the time the mercury had entirely filled the ether bulb, it was judged the apparatus would be filled with pure ether, unmixed with any air. This method of getting the ether gas into the apparatus proved a failure several times for various reasons, but the very close agreement of the two readings which were at length obtained points to their correctness.

MOLECULAR VOLUMES.

L. Meyer¹ gives the following formula for calculating approximate relative molecular volumes, derived from the molecular volume of SO₂, as determined by Andreef at - 8° C.

$$V = 3.10^{-6} \{M(1 + \alpha t)\}^{\frac{3}{2}} \left\{ \frac{1}{\eta} \right\}^{\frac{3}{2}}$$

in which M = molecular weight, t = temperature Centigrade η = coefficient of friction.

The values obtained for the substances under investigation are given on the next page. According to Kopp² the molecular volume of a liquid composed of carbon, hydrogen and oxygen can be found by substituting in its formula 11 for each atom of carbon, 5.5 for each hydrogen and 7.8 for each oxygen. The values thus calculated are given in the last column. The agreement between the molecular volumes calculated in these two ways is quite good, much better than that obtained by L. Meyer and Schumann.

As both apparatus No. 2 and No. 3 gave values for air about 5 per cent. higher than those given by Landolt and Boernstein as probably the most correct values, it is probable that the values of η for the ethers are correspondingly too high. Accordingly in the second table of molecular volumes the values of η were reduced by multiplying by 2,113/2,244, thus calibrating with air, and the molecular volumes recalculated. A still better agreement with Kopp's values is shown, the disagreement being greatest when the boiling point of the ether approaches the temperature at which η was determined.

¹ Wied. Ann., 1881, Bd. 13, p. 17.

² Ann. Chem. Phar., 1855, Bd. 96, pp. 1, 153, 303.

First Table of Molecular Volumes.

Material.	Formula.	Boiling Point in Degrees Centigrade.	$\eta \times 10^7$.	Molec. V. Found.	Molec. V. Calculated According to Kopp.
Di-methyl ether.	C_2H_6O	-23.65	1,190.2	51.62	} 62.8
Ethyl alcohol.	C_2H_6O	78.	1,155.0	55.25	
Methyl-ethyl ether.	C_3H_8O	10. -13.	1,092.3	71.65	} 84.8
Di-ethyl ether.	$C_4H_{10}O$	34.6-35.	1,000	95.73	
Methyl-propyl ether.	$C_4H_{10}O$	40. -45.	1,004.3	95.16	} 106.8
Methyl-isopropyl ether.	$C_4H_{10}O$	7.	1,054.8	88.37	
Ethyl-propyl ether.	$C_5H_{12}O$	66. -68.	916.8	124.19	} 128.8
Ethyl-isopropyl ether.	$C_5H_{12}O$	54. -57.	960.7	115.77	
Di-propyl ether.	$C_6H_{14}O$	84.5-86.5	837.5	158.90	} 150.8
Isopropyl-propyl ether.	$C_6H_{14}O$	76.5-77.	873.4	148.86	
Di-isopropyl ether.	$C_6H_{14}O$	68.5-69.	894.3	144.06	

Second Table of Molecular Volumes.

Material.	Formula.	Boiling Point in Degrees Centigrade.	$\eta \times 10^7$.	Molec. V. Found.	Molec. V. Calculated According to Kopp.
Di-methyl ether.	C_2H_6O	-23.65	1,121.0	56.46	} 62.8
Ethyl alcohol.	C_2H_6O	78.	1,088.0	59.05	
Methyl-ethyl ether.	C_3H_8O	10. -13.	1,029.0	81.12	} 84.8
Di-ethyl ether.	$C_4H_{10}O$	36.6-35.	942.0	104.71	
Methyl-propyl ether.	$C_4H_{10}O$	40. -45.	946.0	104.20	} 106.8
Methyl-isopropyl ether.	$C_4H_{10}O$	7.	993.6	96.66	
Ethyl-propyl ether.	$C_5H_{12}O$	66. -68.	863.6	135.84	} 128.8
Ethyl-isopropyl ether.	$C_5H_{12}O$	54. -57.	905.1	126.61	
Di-propyl ether.	$C_6H_{14}O$	84.5-86.5	788.9	173.08	} 150.8
Isopropyl-propyl ether.	$C_6H_{14}O$	76.5-77.	822.7	163.20	
Di-isopropyl ether.	$C_6H_{14}O$	68.5-69.	842.4	157.51	

In this second table η has been reduced by calibration with air.

MOLECULAR MEAN SPEEDS, FREE PATHS AND COLLISION FREQUENCIES.

In Meyer's Kinetic Theory of Gases on page 219 is given the formula $\eta = 0.30967 \rho L Q$ whence

$$L = \frac{\eta}{0.30967 \rho Q},$$

in which η = coefficient of internal friction of the gas,

ρ = density of the gas,

Q = mean molecular velocity,

L = mean molecular free path.

On page 55 of the same work we find $p = \frac{1}{3} \pi \rho Q^2$ whence

$$Q = \sqrt{\frac{8p}{\pi\rho}},$$

where p = pressure in absolute measure.

On page 195 we see that the

$$\text{Collision Frequency} = \frac{Q}{L}.$$

The values given in the table on this page were calculated according to the above formulæ, at a pressure of 76 cm. of mercury and a temperature of 100° C., the density being calculated from the formula

$$\rho = \frac{1}{3} \frac{(\text{formula weight}) (0.000089)}{1 + \alpha t}.$$

First Table of Mean Molecular Speeds, Free Paths and Collision Frequencies.

Material.	Molecular Weight.	$\eta \times 10^7$.	Mean Molecular Speed Cm. per Sec.	Molecular Free Path Cm. $\times 10^{10}$.	Collision Frequency $\times 10^{-4}$.
Di-methyl ether.	46.048	1,190.2	41,470	61,787	6,711.7
Ethyl alcohol.	46.048	1,155.0	41,470	59,970	6,915.0
Methyl-ethyl ether.	60.064	1,092.3	36,310	49,660	7,312.0
Di-ethyl ether.	74.08	1,000.0	32,695	40,895	7,994.9
Methyl-propyl ether.	74.08	1,004.3	32,695	41,111	7,952.7
Methyl-isopropyl ether.	74.08	1,054.8	32,695	43,180	7,572.0
Ethyl-propyl ether.	88.096	916.8	29,982	34,415	8,711.8
Ethyl-isopropyl ether.	88.096	960.7	29,982	36,063	8,315.5
Di-propyl-propyl ether.	102.112	837.5	27,848	29,201	9,536.6
Isopropyl-propyl ether.	102.112	873.4	27,848	30,454	9,144.6
Di-isopropyl ether.	102.112	894.3	27,848	31,182	8,931.0

Second Table of Mean Molecular Speeds, Free Paths and Collision Frequencies.

Di-methyl ether.	46.048	1,121.0	41,470	58,204	7,125.0
Ethyl alcohol.	46.048	1,088.0	41,470	56,490	7,341.0
Methyl-ethyl ether.	60.064	1,029.0	36,310	46,782	7,762.0
Di-ethyl ether.	74.08	942.0	32,695	38,570	8,477.0
Methyl-propyl ether.	74.08	946.0	32,695	38,725	8,639.5
Methyl-isopropyl ether.	74.08	993.6	32,695	40,682	8,036.7
Ethyl-propyl ether.	88.096	863.6	29,982	32,418	9,248.4
Ethyl-isopropyl ether.	88.096	905.1	29,982	33,976	8,824.3
Di-propyl-propyl ether.	102.112	788.9	27,848	27,507	10,124.0
Isopropyl-propyl ether.	102.112	822.7	27,848	28,685	9,708.0
Di-isopropyl ether.	102.112	842.4	27,848	29,372	9,481.1

In this second table η has been reduced by calibration with air.

It will be noticed that the values are all of the proper order of magnitude, but do not rise and fall in a periodic way while the molecular weight increases, as pointed out for other substances by Meyer on page 196 of his *Kinetic Theory of Gases*, probably because these ethers are all so closely related.

COMPARISON WITH THE RESULTS OF OTHERS.

The results of my work cannot be compared satisfactorily and exactly with that of others, because I have determined the friction at a temperature higher than most other observers, and the law of its increase with the temperature is not accurately known in each case. Furthermore, air, di-ethyl ether, di-methyl ether and ethyl alcohol are the only substances which I have employed that others have investigated.

Disregarding the results with apparatus No. 1 as being only preliminary, we see that the values of η for air for the other two pieces of apparatus agree closely and are consistent, though both are about 5 per cent. higher than the values which are most probably correct, according to Landolt and Boernstein's tables. That the relative values of η at the different temperatures are correct is shown by calculating η at 0° C. by Sutherland's formula¹ and then calculating from that η at 100° C. Using the value of the cohesion constant $C = 119.4$ as determined by Breitenbach² we get for apparatus No. 2, $\eta_0 = .0001793$ and $\eta_{100} = .00022367$ the latter value agreeing with .0002242 observed within $\frac{1}{4}$ per cent. For apparatus No. 3 we get in like manner $\eta_0 = .0001795$ and $\eta_{100} = .0002239$, the latter value agreeing with .0002246 observed within $\frac{1}{3}$ per cent. This agreement is within the limits of error of the experiments.

Puluj's³ formula for the coefficient of friction of di-ethyl ether vapor, $\eta = 0.0000689 (1 + .0041575 t)^{.94}$ gives $\eta = 0.0000935$ at 100° C. which agrees with my corrected value of 0.0000942 within $\frac{3}{4}$ per cent. This is good agreement bearing in mind the fact that Puluj's formula was determined from experiments over a small range of temperature, viz. : from 0° to 37° C.

¹ *Phil. Mag.*, 1893 (5), vol. 36, p. 507.

² *Drude's Ann.*, 1901, Bd. 5, p. 166.

³ *Wien. Ber.*, 1878, vol. 78 (2), p. 279; *Carls Rep.*, 1878, vol. 14, p. 573; *Phil. Mag.*, 1878 (5), vol. 6, p. 157.

The coefficient of friction of di-methyl ether is given on page 192 of Meyer's Kinetic Theory of Gases as 0.000092 at 0° C. No one has determined the law of its increase with the temperature. My corrected value is .0001121 at 100° C. which seems reasonable.

Steudel¹ gives 0.000142 as the coefficient of friction of ethyl alcohol at 78.4° C., its boiling point. My corrected value of .0001088 at 100° C. does not agree well with this. Because his value was determined at the boiling point I think it is open to question. My value for ethyl alcohol agrees much better with Puluj's¹ results which are 0.0000827 at 0° C. and 0.0000885 at 16.8° C. He assumes η is proportional to the absolute temperature which gives $\eta = .0001130$ at 100° C., which is nearly 4 per cent. higher than my value of .0001088. I think the assumption that η increases exactly as the absolute temperature is not strictly correct.

Concerning the differences which I have found between the normal propyl and the isopropyl ethers I would point out that Lothar Meyer, Schumann and Steudel found similar differences between many, though not all, of the normal propyl and isopropyl compounds which they examined. They also found that normal butyl, isobutyl and tertiary butyl compounds showed still more regular differences. The weight of evidence gives a larger molecule to the primary, a smaller to the secondary and the smallest to the tertiary compound. My values of the molecular speeds, free paths and collision frequencies being for 100° C. of course do not agree with those calculated for 0° C. by others.

SUMMARY OF RESULTS.

1. The coefficients of internal friction of the following eight ether gases which have hitherto not been experimented with, have been determined with considerable accuracy as follows :

Methyl-ethyl ether.....	0.0001029	at 100° C.
Methyl-propyl ether	0.0000946	“ “
Methyl-isopropyl ether ...	0.00009936	“ “
Ethyl-propyl ether.....	0.00008636	“ “
Ethyl-isopropyl ether.....	0.00009051	“ “
Di-propyl ether	0.00007889	“ “
Iso-propyl-propyl ether.....	0.00008227	“ “
Di-isopropyl	0.00008424	“ “

¹ Wied. Ann., 1882, Bd. 16, p. 369.

2. The molecular volumes calculated from the friction have been shown to agree fairly well with those obtained by Kopp's rule.

3. A marked and unmistakable difference between the normal propyl and isopropyl ethers has been found, proving that the difference in the molecular structure of these ethers has a very noticeable effect upon their internal friction, and therefore upon the size of their molecules, the molecules having the most numerous branches being smaller than those with fewer or no branches.

In conclusion I wish to express my thanks to Professor Loeb for suggesting both the subject of this research and the form of apparatus, and for his kind interest and help throughout the course of the investigation. In addition I wish to thank him heartily for his courtesy in supplying me with certain of the necessary ethers.

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THE DISTRIBUTION OF ENERGY EMITTED BY A
RIGHI VIBRATOR.

BY C. R. FOUNTAIN AND F. C. BLAKE.

INTRODUCTION.

HERTZ¹ found that most of the energy emitted by his oscillator was radiated in the equatorial plane, that is, the plane through the spark gap and perpendicular to the axis of the oscillator; and that little or no energy was radiated in the polar direction. He mapped the direction of the electric force about the oscillator, but his results were qualitative rather than quantitative on account of the type of detector used.

In developing the theoretical side Hertz² failed to take into account the damping of the waves, which V. Bjerkness,³ Hull⁴ and others have shown to be large. Karl Pearson and Alice Lee⁵ have shown how this factor would affect the drawings which Hertz made to represent the field about the oscillator. But they neglected the fact that there is an electrostatic field about the oscillator before the oscillation begins. A. E. H. Love⁶ has considered theoretically all these factors and shown how the electric and magnetic forces may be computed for any point in the field.

It is the purpose of the present paper to show the relative amounts of energy radiated in the various directions about a Righi vibrator, and to indicate what bearing the experiments to be described have upon existing theories.

APPARATUS.

The general arrangement of the apparatus is shown in Fig. 1. The vibrator *V* is placed at the center of the circle *H*. The distance

¹ Electric Waves, Eng. ed., p. 87.

² Electric Waves, Eng. ed., p. 141.

³ An. der Phys., Vol. 44, pp. 81 and 513.

⁴ Phys. Rev., Vol. 5, p. 231, 1897.

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r of the receiver R is varied by sliding along a meter bar MM' . The angle which the radius vector at any point makes with the equatorial (vertical) plane could be varied by swinging the circle H about the axis NN' and its position at any time could be read on a graduated disk DD' . This angle will hereafter be denoted by θ .

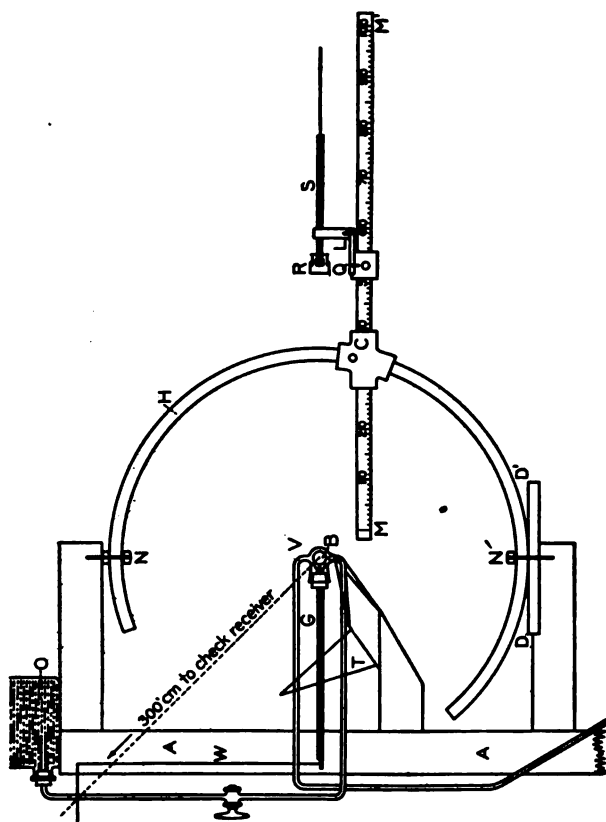


Fig. 1.

The vertical angle could be changed by sliding the clamp C about the graduated circle H . At any point the orientation of the receiver R could be changed by rotating the rod S about its axis and also by rotating the support arm L about the pivot Q . All the parts shown are drawn to scale and can be compared with the meter bar MM' . The large bottle of oil, O , on top of the support AA' supplied a constant stream of olive oil between the vibrator balls BB'

to carry off any carbon particles formed by the electrical decomposition of the oil. The brass balls BB' , 2.54 cm. in diameter, were sealed with ordinary red sealing wax to the enlarged ends of the glass tubes G . These were fitted into the glass vessel V . The wires W from a 10-inch induction coil passed through the tubes G and terminated in small beads about .3 cm. from the balls B . This permitted the balls to be charged by small sparks through air. The

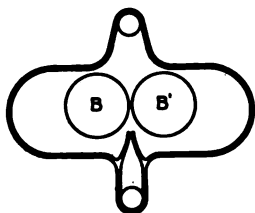


Fig. 2.

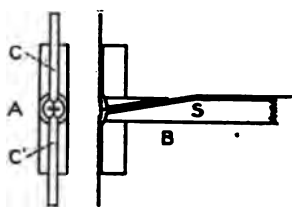


Fig. 3.

oscillation between the balls BB' took place through a small film of olive oil. An enlarged view of a vertical cross-section through the axis of the vibrator is shown in Fig. 2. This view shows the relative positions of the balls in the glass vessel. The tubes G led directly back so as to affect as little as possible the field in front of the vibrator. The triangular block T was placed to prevent interference with waves reflected from the post AA' . No metallic nails were used in constructing the apparatus.

RECEIVER.

The wave-detector was the type of thermo-element used in a former paper,¹ differing mainly in dimensions, but the contact between the iron and constantan wires was electrically welded instead of soldered. Fig. 3 shows two views of the receiver and R , Fig. 1, gives an end view showing the cardboard box surrounding it. The iron and constantan wires each .0025 cm. in diameter were soldered to the copper strips CC' (Fig. 3, A) crossed in the center and soldered to small copper wires which were drawn backward through the rod S (Fig. 3, B) so as to leave as little as possible (about .15 cm.) of the wires projecting at right angles to the axis of the copper strips. The total length of the receiver was 8 cm.

¹ Blake and Fountain, *PHYS. REV.*, Vol. XXIII., No. 4, p. 257, 1906.

The strips CC' were .3 cm. wide and the length of wire between them was .35 cm.

Since a vibrator does not always give off the same amount of energy a check receiver was employed and the relative amounts of energy denoted by the ratios M/C , where M denotes the scale reading for the galvanometer connected to the main receiver and C the corresponding reading for the check receiver. To keep the two receivers from affecting each other the check receiver was placed on a shelf 3 meters distant near the focus of a spherical metallic mirror of 25 cm. diameter and 16 cm. focal length.

The same induction coil and galvanometers used in an earlier experiment¹ served in the present study.

TESTS FOR DISTURBING FACTORS.

Before beginning the exploration of the field it was necessary to make sure that no disturbing factors were neglected. A few of the more important tests are here given :

1. When the two spheres B, B' were made to touch each other and the induction coil put in operation, no effect could be detected in either galvanometer unless one of the receivers was within 10 cm. of a lead wire W .

2. Notwithstanding this a further test for effects from the induction coil was made by taking readings with the coil in various orientations at its regular distance of 400 cm. from the vibrator and 900 cm. from the galvanometers. The greatest variation in the ratios M/C , even when the main receiver was at the pole so as to receive but little of the energy radiated from the vibrator, was less than 5 per cent. The coil was then placed permanently in the position to give least effect.

3. The vibrator axis was set obliquely to the walls of the room so as to avoid all chance of stationary waves and disturbing reflections. Later tests showed the complete absence of any energy reflected from surrounding objects except a small amount reflected from the post AA' , Fig. 1. The triangular block T was inserted to divert these reflections.

4. The ratio M/C should be constant for all points equidistant in

¹ Blake and Fountain, l. c.

the equatorial plane. This was true for all angles from 45° below the horizontal to 85° above, except in the neighborhood of 45° above when an increase of nearly 4 per cent. was observed for a distance of 20 cm. For this region however it was impossible to cut off the reflections from the post AA' without interfering with the waves en route to the check receiver.

5. One of the most troublesome disturbances and one not discovered for some time was the effect of one receiver upon the other. Further experiments showed that a copper strip, the same length as a receiver, when placed in the vicinity of the vibrator might increase or decrease the ratio M/C by 50 per cent. In other words the receivers reradiate most of the energy they receive. It was for this reason that the check receiver was placed so far away near the focus of a spherical mirror. It was slightly displaced from the focus so that the energy reradiated from it would be brought to a focus somewhere above the horizontal plane. If the main receiver were 5 cm. from the vibrator the energy reradiated from it would be brought to focus sufficiently near the check receiver to nearly double its readings. If placed 10 cm. away, however, the effect could scarcely be detected. But to make sure that no effect of this kind should enter the final readings no attempt has been made to explore the field within a distance of 14.4 cm.

6. The galvanometer wires leading to the thermal junction were closely twisted to within about .7 cm. from the thermal junction. But if these twisted wires formed a loop where the field was strong and projected in the direction of the electric force it might absorb nearly as much energy as the receiver itself. That is, if the receiver axis were perpendicular to the electric force and a loop of about 3 cm. diameter were parallel to the electric force, the galvanometer deflection might be nearly as large as when the receiver was in the position to absorb the most energy. These lead wires had therefore to be carefully straightened.

7. Another effect mentioned in a former paper¹ as the aging of the vibrator had to be taken into account. The ratio M/C does not remain constant for successive readings when the positions of the receivers remain the same. After the vibrator had been cleaned

¹ Blake and Fountain, l. c.

TABLE I.

*Swinging Curve at 15 cm. August 7, 1906, 2 P. M.**Resistance of main = 1.749 ohms. Skunts, 6 and 10.**Resistance of check = 1.889 ohms. Receiver faced,**Standard value for 0-0-15 is 27.80.*

Main.			Check.			Ratio.			
Zero.	Turning Point.	Def.	Zero.	Turning Point.	Def.	M C	Mean.	Standard Mean.	Correct'd Mean.
	0-0-15								
406	44	362	159	72	87	4.17			
404	54	350	157	74	83	4.22	4.20	6.62	27.80
	0-15-15								
408	75	333	158	74	84	3.97—			
407	157	250	158	95	63	3.97	3.97		26.18
	0-345-15								
402	20	382	156	63	93	4.11			
403	40	363	157	69	88	4.13	4.12		27.02
	0-0-15								
402	58	344	155	74	81	4.25			
403	12	391	155	63	92	4.25	4.25	6.54	27.80
	0-60-15								
401	281	120	153	73	80	1.50			
404	304	100	155	88	67	1.49	1.50		9.70
	0-300-15								
401	288	113	152	72	80	1.41+			
402	281	121	152	67	85	1.42+	1.42		9.08
	0-0-15								
402	73	329	149	74	75	4.38			
399	82	317	150	78	72	4.40	4.39	6.33	27.80
	0-30-15								
403	113	290	153	71	82	3.54			
404	98	306	155	69	86	3.56	3.55		22.40
	0-45-15								
402	192	210	154	75	79	2.66			
401	202	199	154	79	75	2.65+	2.66		16.75
	0-0-15								
399	43	356	153	72	81	4.39			
401	36	365	155	73	82	4.45	4.42	6.29	27.80
	0-75-15								
401	360	41	153	84	69	.594			
400	358.5	41.5	153	84	69	.602	.598		3.74
	0-90-15								
400	391	9	154	72	82	.110			
400	390	10	154	66	88	.114	.112		.69
	0-0-15								
398	55	343	152	76	76	4.52			
402	53	349	155	78	77	4.53	4.52	6.15	27.80

and bright surfaces of the balls brought into the sparking position, the ratio M/C would either steadily increase or decrease according to circumstances. But after it had been run for sometime this variation was no longer a steady one. In the former paper we offered a possible explanation of this which seemed to fit all our earlier observations. However, later observations showed that the explanation was far from complete; for when a rigid test was made,

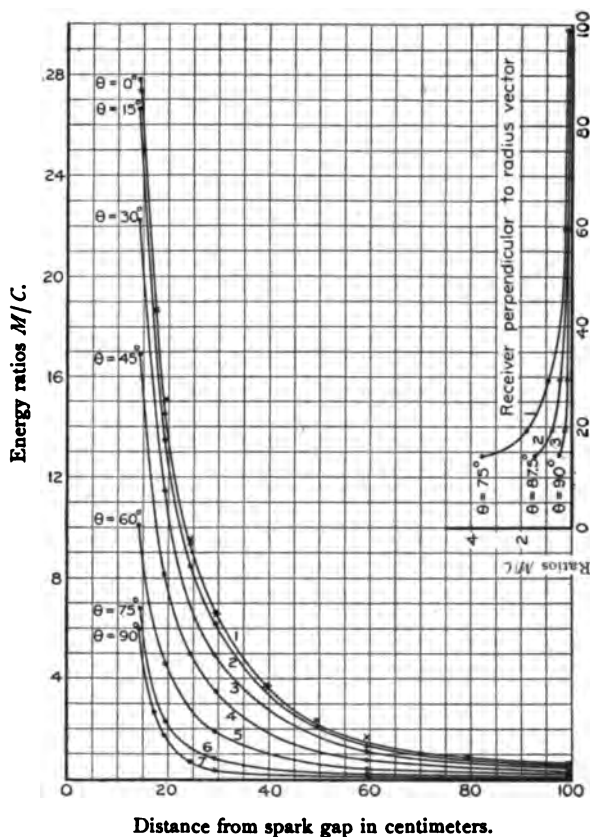


Fig. 4. The angle θ opposite the first point on each curve represents the angle between the radius vector and the equatorial plane. The orientation of the receiver is such that maximum energy is received. The crosses indicate points for curve 1 as calculated from the empirical formula in Table II.

the ratio M/C steadily decreased for conditions which seemed identical with those which had previously shown the greatest increase.

Fig. 5. Distance from spark gap in centimeters.

At present it seems probable that the wearing away of the balls at the spark gap causes a slight change in the wave-length emitted. Unless the two receivers are tuned to exactly the same wave-length, any change in the wave-length emitted will affect each receiver differently, thus changing the ratio M/C . But whatever the cause may be the effect had to be taken into account. Since

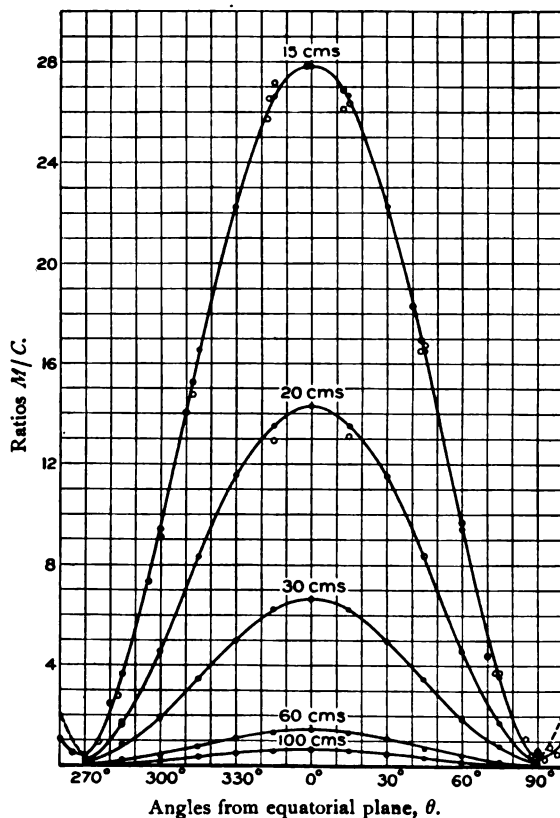


Fig. 6. In each curve the receiver is at a constant distance from the spark-gap. The receiver's axis is always perpendicular to the radius vector. Black dots show mean of all observations for a given angle from the equatorial plane. Circles show individual observations which gave greatest variation from this mean.

the variation showed itself to be a definite linear one for a short time after the vibrator was cleaned, a standard position for the main receiver was chosen and returned to after every fourth setting. The ratios for the intermediate positions were allowed

their percentage increase or decrease as shown by the two values for the standard position. To get a complete curve before the deterioration became variable only two or three readings were taken for each setting.

The effective resistance of the thermal junctions varied with the temperature of the room, therefore the ratios M/C for any one posi-

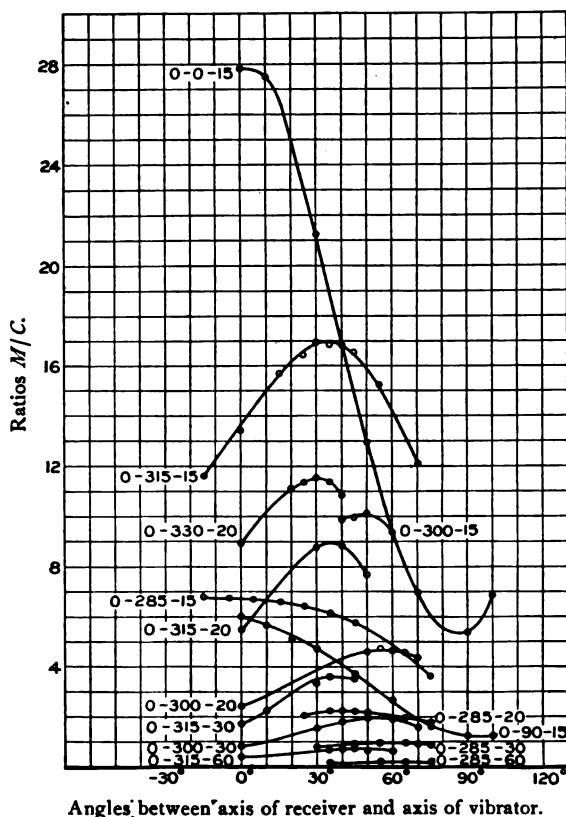


Fig. 7. The orientation of the receiver is changed while its position in the field remains constant.

tion varied from day to day. This ratio also depended upon the galvanometer shunts used. A standard value (27.80) was chosen for the position (0°-0°-15 cm.) of the main receiver. The first figure in denoting the position of the receiver refers to the angle from the horizontal plane measured on the vertical circle H . The second figure denotes the angle from the equatorial plane, that is

the angle θ . The last figure shows the distance (r) in cms. of the middle of the receiver from the spark gap.

The preceeding sample set of observations shows how the various corrections were made to the observed ratios.

EXPERIMENTAL RESULTS.

Curve 1, Fig. 4, is the standard curve upon which all other curves are based. The receiver was kept in the horizontal and equatorial planes while the distance alone was varied. The ratios here determined for the various distances are used as the standard values for all the swinging curves in Fig. 6.

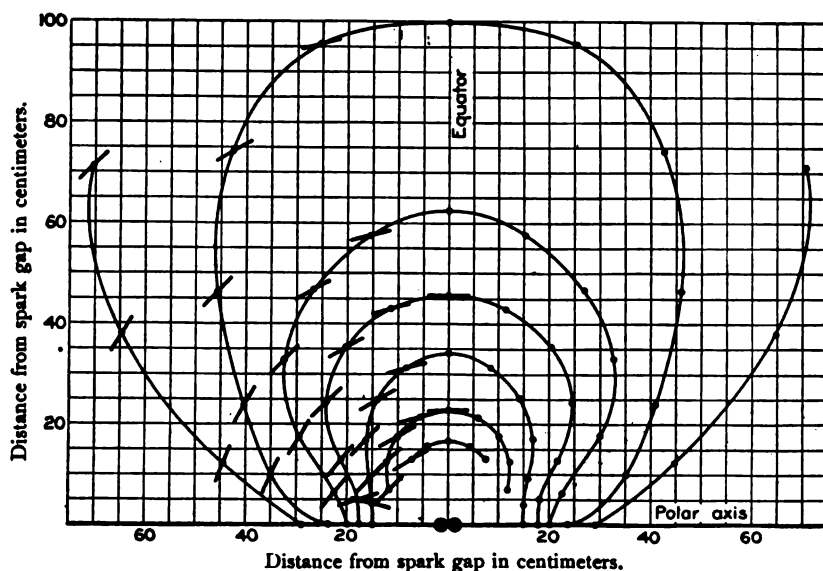
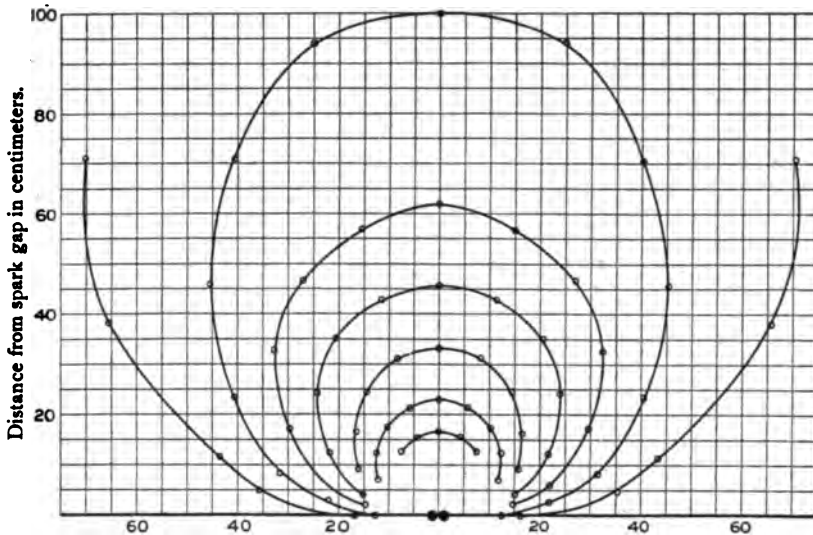


Fig. 8. Equi-energy curves.

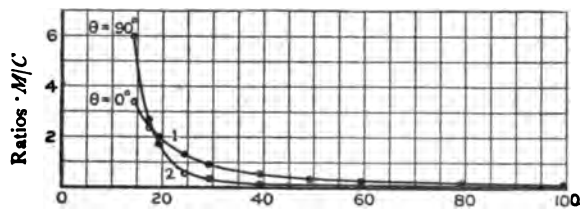
The direction curves, Fig. 7, show the direction of the resultant electric force at the various points and the maximum values for such positions. Curves 2 to 6, Fig. 4, were obtained by a combination of the curves in Fig. 7 with those in Fig. 6. The curves in Fig. 5 were obtained directly from those in Fig. 6. The points on the equi-energy curves in Fig. 8 were found by taking arbitrary values for the ratios and ascertaining from the curves in Fig. 4 at what distance those ratios would be found for various angles. That is, Fig. 8 shows the electric field in the horizontal plane

through the vibrator plotted with lines drawn through points which receive the same amount of energy. Each curve runs through the positions at which the energy intensity is twice that for points lying on the curve next beyond it. In one half of the field the orienta-



Distance from spark gap in centimeters.

Fig. 9. Equi-energy curves. Receiver everywhere perpendicular to radius vector. tion of the receiver for maximum energy is shown. In general this direction is at right angles to the radius vector at that point. In the polar direction ($\theta = 90^\circ$), however, this is not true, nor is it



Distance from spark gap in centimeters.

Fig. 10. Radial distance curves.

true for some of the other angles when the receiver is near the vibrator. For example, when $\theta = 75^\circ$ the axis of the receiver must be directed toward the vibrator when $r = 15$ cm., but conforms to the general rule when $r > 50$ cm.

TABLE II.

Assume $E = K^2 \frac{\cos^2 \theta}{r^2} + k^2 \frac{\sin^2 \theta}{r^2}$, where $K = 75.25$, $k = 495$.

Distance. r	$\theta = 0^\circ$		$\theta = 15^\circ$		$\theta = 30^\circ$		$\theta = 45^\circ$		$\theta = 60^\circ$		$\theta = 75^\circ$		$\theta = 90^\circ$	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
14.4	27.80	27.30	26.65	25.91	22.25	21.84	16.90	16.47	10.11	11.10	6.80	7.11	5.98	5.65
17.4	18.70	18.70		17.36		14.68		10.67		6.65		3.72	2.63	2.64
19.4	14.50	15.04	13.48	14.19	11.45	11.71	8.17	8.38	4.58	5.04	2.22	2.60	1.73	1.71
24.4	9.36	9.51	8.58	8.94		7.31	4.95	5.10		2.89		1.28	.65	.68
29.4	6.63	6.55	6.20	6.15	4.91	5.00	3.44	3.44	1.86	1.88	.85*	.75	.32	.33
39.4	3.74	3.65		3.42		2.77		1.88		.99		.34	.12	.10
49.4	2.03	2.32		2.17		1.75		1.18		.61		.19		.04
59.4	1.43	1.69	1.31	1.50	1.09	1.20	.72	.81	.40	.42	.18	.13	.05	.02
79.4	.92	.90		.84		.68		.45		.23		.07		.008
99.4	.62	.57	.59	.53	.47	.43	.34	.29	.19	.14	.10	.04	.03	.003

In Fig. 9 the equi-energy curves are drawn just as in Fig. 8, except that the receiver has its axis everywhere perpendicular to the radius vector. The curves in Fig. 5 must here be used instead of curves 6 and 7 of Fig. 4.

When $\theta = 0$ and the axis of the receiver is radial the energy absorbed is shown in curve 1, Fig. 10, while curve 2 shows the effect when the receiver is radial in the polar axis ($\theta = 90^\circ$).

The polarization of the waves seems to vary with the distance from the vibrator. Thus at 0-0-15 only 2.7 per cent. as much energy was found when the receiver was perpendicular to the horizontal plane as when it was perpendicular to the equatorial plane. For 0-0-30 the corresponding percentage was 4.6, while at 0-0-60 it was 9.7 per cent.

An empirical formula was found to represent approximately the maximum energy for any point in the field. Table II. shows the corresponding observed and calculated values. The degree of agreement between this formula and the one developed later from purely theoretical considerations will be discussed later.

For points where there is only a very small amount of energy the deflections of the galvanometers due to magnetic and other disturbances render the observations quite inaccurate. That part of Table II. enclosed within the heavy lines includes those observations which are apt to be especially inaccurate. The position marked with a star (*) is not trustworthy because the only readings taken at that point were at a time when the deterioration factor was quite large and irregular. The energy recorded for that part of the field near the vibrator where the radial and the transverse components of the forces have about the same effect will probably be too small, for the receiver cannot be turned so as to get the full effect of either force.

THEORETICAL DISCUSSION.

Assuming that the field about a Righi vibrator is similar to the field about a theoretical electric doublet the forces in the field may be represented as has been done by A. E. H. Love.¹ That is the transverse component of the electric force is

¹ A. E. H. Love, Proc. Royal Soc., Vol. 74, p. 73, 1904.

$$F = \frac{\cos \theta}{r^3} A e^{-\frac{\nu}{\lambda}(\alpha-r)} \left[\left(1 - \frac{r\nu}{\lambda} + \frac{r^2(\nu^2 - 4\pi^2)}{\lambda^2} \right) \sin \frac{2\pi}{\lambda} (ct - r + \epsilon) + \frac{2\pi r}{\lambda} \left(1 - \frac{2r\nu}{\lambda} \right) \cos \frac{2\pi}{\lambda} (ct - r + \epsilon) \right], \quad (1)$$

when $ct > r$, and when $ct < r$ it is

$$F = \frac{\cos \theta}{r^3} A \sin \frac{2\pi\epsilon}{\lambda}. \quad (2)$$

Where θ is the angle between the radius vector and the equatorial plane, r the distance along the radius vector, A a constant depending upon the amplitude of vibration, ν the damping constant, λ the wave-length, c the velocity of radiation, t the time from the beginning of the oscillation, and ϵ a constant depending upon the phase between the electric and magnetic forces.

The radial component of the electric force is

$$R = \frac{2 \sin \theta}{r^3} A e^{-\frac{\nu}{\lambda}(\alpha-r)} \left[\left(1 - \frac{r\nu}{\lambda} \right) \sin \frac{2\pi}{\lambda} (ct - r + \epsilon) + \frac{2\pi r}{\lambda} \cos \frac{2\pi}{\lambda} (ct - r + \epsilon) \right], \quad (3)$$

when $ct > r$, and

$$R = \frac{2 \sin \theta}{r^3} A \sin \frac{2\pi\epsilon}{\lambda}, \quad (4)$$

when $ct < r$.

The transverse component of the magnetic force is

$$H = -\frac{\cos \theta}{r^2} A e^{-\frac{\nu}{\lambda}(\alpha-r)} \left[\left(\frac{\nu}{\lambda} - \frac{r(\nu^2 - 4\pi^2)}{\lambda^2} \right) \sin \frac{2\pi}{\lambda} (ct - r + \epsilon) - \frac{2\pi}{\lambda} \left(1 - \frac{2r\nu}{\lambda} \right) \cos \frac{2\pi}{\lambda} (ct - r + \epsilon) \right], \quad (5)$$

when $ct > r$, but vanishes for $ct < r$.

The radial component of the magnetic force is everywhere equal to zero.

If these represent the true values for the forces, the current produced by them at any point in a conductor placed in the field can be determined. Consider the receiver in the equatorial plane with its axis parallel to the axis of the vibrator. The forces in the field

are practically the same about every point in the receiver. So the average force about the receiver is proportional to the force at any particular point in it, if it be more than 14 cm. from the vibrator. The current at any point in the receiver will be proportional to the forces about any particular point in it. That is, the rate of change with the distance is practically the same for all the forces about the receiver. Therefore the current at the thermal junction will be proportional to the forces in the immediate neighborhood of the junction. The deflections of the galvanometers will be proportional to the heat developed at the thermal junction; that is, proportional to the square of the current at the junction.

$$\therefore \text{Heat} \propto \int_0^{\infty} i^2 dt \propto \int_{r/c}^{\infty} (F^2 + H^2) dt.$$

Since $\tan 2\pi\epsilon/\lambda = 2\pi/\nu$,¹

$$\int_{r/c}^{\infty} (F^2 + H^2) dt = \frac{\cos^2 \theta}{r^2} A^2 \frac{2\pi^2}{c\nu\lambda^3} (4\pi^2 + \nu^2) \left[1 - \frac{2\nu\lambda^3}{r^2(4\pi^2 + \nu^2)^2} + \frac{\lambda^4(4\pi^2 + 5\nu^2)}{2r^4(4\pi^2 + \nu^2)^3} \right]. \quad (6)$$

Within the region explored the last two terms in the brackets could never be larger than .0002. Therefore the electromagnetic energy, will be approximately proportional to $\cos^2 \theta/r^2$. This is identical with the empirical equation in Table II.

Let us now consider what effect the radial forces will have upon the receivers. If the main receiver is in the polar region ($\theta = 90^\circ$) with its axis parallel to the radius vector the only force acting along its axis will be the radial component of the electric force. Again assuming that the current at the junction is proportional to the forces immediately surrounding that point, the energy absorbed will be proportional to

$$\int_{r/c}^{\infty} R^2 dt = \frac{A^2\pi}{2c\nu\lambda} \frac{\sin^2 \theta}{r^4} \left[1 - \frac{\lambda}{r} \frac{4\nu}{(4\pi^2 + \nu^2)} + \frac{\lambda^2(4\pi^2 + 5\nu^2)}{r^2(4\pi^2 + \nu^2)^2} \right]. \quad (7)$$

Calculating the value of ν from the interference curves obtained by Willard and Woodman¹ for waves 20 cm. long it seems probable that the value of ν is not greater than .15. Substituting this value

¹See Love, l. c.

in (7) the last two terms in the brackets become larger than .02 for $r = 15$ cm. but only .001 when $r = 30$ cm.

The values in the last column of Table II. were calculated from the equation $E = k^2/r^4$, where k was 495. If the last two terms of (7) be introduced and k be given the value 489 the figures for the last column of Table II. become respectively, 5.72, 2.65, 1.71, .68, .32, .10, .04, .02, .008, .003. These show a slightly better agreement with the observed values. The value assumed for ν is prob-

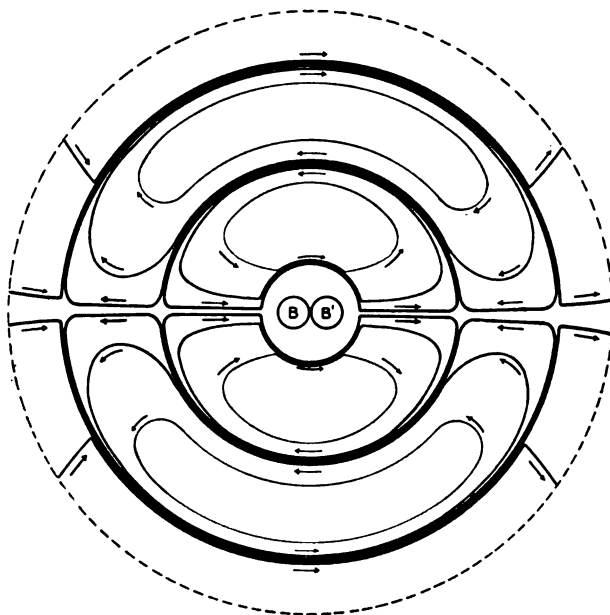


Fig. 11. Lines of electric force.

ably too large. A smaller value would give still better agreement.

The assumption that the current at the junction is proportional to the forces at that point is probably not strictly true. When $r = 15$ cm. the value of R at the center of the receiver is certainly not proportional to the average value of R for the entire length of the receiver. As the charges begin to build up at the ends of the receiver the forces of their mutual repulsion increase so as to oppose the force R with increasing effectiveness for increasing distance from the center of the receiver. To compute the

effect of these repulsive forces would require a better knowledge of the number of free electrons in the copper strips and their behavior under oscillating forces than the authors have at present. Some idea of the extent to which these forces counteract the effect of the forces in the field near the ends of the receiver may be seen by neglecting these forces and computing the ratio of energy absorbed when $r = 15$ cm. to that absorbed when $r = 30$ cm. There is a 40 per cent. variation from the observed ratio. The error involved for the corresponding distances in assuming that the current at the junction is proportional to the value of R at that point is probably less than 4 per cent.

The physical significance of the radial force may be seen from Fig. 11, where the lines of force are plotted for

$$t = \frac{\frac{3}{2}\lambda - \epsilon}{c}.$$

The three values for the intensity of the force here plotted are to each other as 10,000 : 100 : 10. The dotted circle is $\frac{3}{2}\lambda$ from the spark-gap. Lines are drawn up to a distance of $\frac{1}{4}\lambda$ although the formula used probably does not hold so near to such a vibrator. As the energy flows into the polar region from the two halves of the field the electric forces in the two approaching waves will always be in the same relative direction. But since the direction of the energy flow is opposite in the two cases the magnetic forces must be opposed to each other. Therefore if the two halves of the field were symmetrical there would be at any point on the polar axis a varying electric force, but the resultant magnetic force would always be equal to zero. Prof. G. F. FitzGerald¹ made this case the basis of an article on the "Longitudinal Component in Light."

When the receiver is in the polar region ($\theta = 90^\circ$) with its axis perpendicular to the polar axis the energy absorbed varies approximately as $1/r^4$ and therefore might suggest that it was due to some effect of the force R upon the lead wires. Varying the positions of the lead wires produced only slight changes in the energy absorbed. The transverse components of the electric and magnetic forces become equal to zero when $\theta = 90^\circ$. But the ends of a receiver 8

¹ Phil. Mag., Vol. 42, p. 266, 1896.

cm. long reach out on either side into the field where there is a force component toward the middle of the receiver. This is readily seen from Fig. 11. The forces at the two ends would at the same instant be both directed toward the center so that the only flow must be from the ends of the receiver past the thermal junction into the capacity of the galvanometer circuit and out again. If such a current were proportional to the forces at the ends of the receiver the heat developed at the junction would vary approximately as shown in curve 3, Fig. 5. The whole effect is so small that its exact nature is very difficult to determine.

When θ is 0° and the receiver radial the energy absorbed varies as $1/r^2$, that is in the same way as when the receiver is perpendicular to the radius vector. Varying the lead wires failed to reveal the cause for an absorption of energy as great as shown by curve 1, Fig. 10. The radial component of the electric force should be zero for this position, and the axis of the receiver is perpendicular to both the electric and magnetic forces. No satisfactory explanation for this phenomenon has yet been found.

CONCLUSIONS.

The results of the present investigation seem to indicate :

1. That in computing the total energy in the field about a Righi vibrator it is necessary to consider the radial component of the electric force as well as the transverse components of the electric and magnetic forces.
2. That the electromagnetic waves spread out from the spark gap in such a manner that the energy at any point is approximately proportional to the square of the cosine of the angle between the radius vector and the equatorial plane and inversely proportional to the square of the distance from the spark gap.
3. That the energy due to the radial component of the electric force varies approximately as the square of the sine of the angle between the radius vector and the equatorial plane and inversely as the fourth power of the distance from the spark gap.
4. That in order to receive the maximum energy the thermal element of the Klemenčič type should everywhere be perpendicular to the radius vector except near the poles, where it should be parallel to the radius vector.

5. That the thermal element used in these experiments when placed in the equatorial plane with its axis parallel to the direction of propagation of the electromagnetic waves absorbs more than 14 per cent. as much energy as when it is in the resonating position.

6. That this type of receiver absorbs a small amount of energy when it is on the polar axis and perpendicular to it, and therefore perpendicular to the radius vector.

7. That two such receivers in the same field greatly influence each other.

8. That a Righi vibrator does not continue to give out wave-trains of the same strength or character as shown by its "deterioration" with use.

9. That the waves from a Righi vibrator appear to become less plane polarized as they proceed from the vibrator.

10. That a theory based upon the assumption that the waves from a Righi vibrator are identical with those from a vibrating "electric doublet" and also that the thermal element of the Klemenčič type acts as a "point receiver" holds with a fair degree of accuracy up to within $\frac{1}{4}\lambda$ from the vibrator.

We wish to thank Mr. J. B. Blanchard and others for their assistance in taking measurements. To Professor Hallock and Professor Wills we are indebted for their suggestions and friendly interest. Our acknowledgments are especially due to Professor E. F. Nichols who suggested the problem and some of the methods for solving it.

PHENIX PHYSICAL LABORATORIES,
COLUMBIA UNIVERSITY,
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A STUDY OF THE REVERSIBLE PENDULUM.¹

PART I: THEORETICAL CONSIDERATIONS.

BY JOHN C. SHEDD AND JAMES A. BIRCHBY.

IF the entire mass of a compound pendulum be M and its radius of gyration about the centroid of the pendulum be a , its moment of inertia about the centroid is Ma^2 and its moment of inertia about a parallel axis at a distance z is $M(a^2 + z^2)$. If this second axis be taken as the center of support of the pendulum, then its equivalent length is

$$l = z + \frac{a^2}{z}. \quad (1)$$

Solving for z the expression is had,

$$z = \frac{1}{2}(l \pm \sqrt{l^2 - 4a^2}). \quad (2)$$

From this it appears that for any given equivalent length there are in general two possible positions of the supporting knife edge with reference to the centroid, *i. e.*,

$$\left. \begin{aligned} z_1 &= \frac{1}{2}(l + \sqrt{l^2 - 4a^2}) \\ z_2 &= \frac{1}{2}(l - \sqrt{l^2 - 4a^2}) \end{aligned} \right\}. \quad (3)$$

If the pendulum be provided with two knife-edges k_1 and k_2 , then the equivalent lengths from the respective knife-edges are

$$\left. \begin{aligned} l_1 &= z_1 + \frac{a^2}{z_1} \\ l_2 &= z_2 + \frac{a^2}{z_2} \end{aligned} \right\}. \quad (4)$$

and

¹ Read before joint meeting of the Am. Phys. Soc. and Section B of the A. A. A. S., New York, December 29, 1906.

These lengths will in general be different in value but it is of course possible that $l_1 = l_2$.

If this be the case, then $a^2 = z_1 z_2 (z_1 - z_2) / (z_1 - z_2) = z_1 z_2$, provided (in general) that $z_1 \neq z_2$. It is thus seen that the radius of gyration is the mean proportional between the segments (z_1 and z_2) into which the centroid divides the distance between the knife-edges.

Substituting the value $z_1 z_2$ for a^2 in the expression for l_1 and l_2 it is seen that

$$l_1 = l_2 = z_1 + z_2,$$

showing that the equivalent length now becomes the distance between knife-edges. Since a is the mean proportional between z_1 and z_2 , it is apparent that its value cannot exceed

$$\frac{1}{2}(z_1 + z_2), \text{ or } \frac{1}{2}L.$$

If this condition with respect to a be not fulfilled, the same period cannot be secured from both knife-edges, and the pendulum cannot be brought into proper adjustment.

The fact that it is possible to realize the condition $l = z_1 + z_2$ was made use of by Captain Kater in 1817, and constitutes the basis of the reversible pendulum bearing his name. Since then the general theory of the compound pendulum up to the point that Kater applied it has been completely worked out and may be found in various works on mechanics. This also includes a discussion of precautions and corrections necessary when the pendulum is used as an instrument of precision. In a recent article¹ Dr. R. R. Tatnall has somewhat extended the theoretical discussion to cover a number of important points. In the present paper it is proposed to discuss the equation of the pendulum from both the analytical and graphical standpoints, and also the various possible methods by which the pendulum may be used. Under the latter head several novel modifications will be pointed out.

From equation (1), together with the definition of z , it is seen that l (and therefore the period of the pendulum), is independent of the direction in which z is measured, provided only that it lie in a plane passing through the centroid of M and normal to the axis

¹ PHYSICAL REVIEW, VOL. XVII., 1903. See also A. O. Allen, *Math. Gazette*, Vol. III., 1906.

about which the moment of inertial is taken. Two circles may thus be drawn about the centroid (Fig. 1, C) having radii equal to z_1 and z_2 respectively, and all points on either of these circles taken

as points of suspension will give the same equivalent length, and hence the same period for the pendulum. The values of the radii of these circles are given by equations (3). In practice the points A , B , D and E are the only points realizable and it is seen that for every compound pendulum there are four such points having the same equivalent length and the same period. The value of this common period is,

$$t = \pi \sqrt{\frac{I}{g}} \quad (5)$$

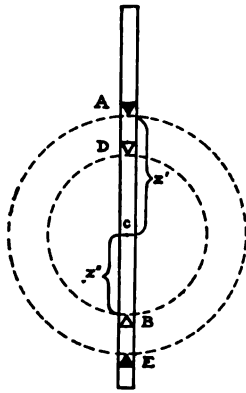


Fig. 1.

In general experimental work the point A is taken as fixed by one knife-edge and the other knife-edge is moved until experimentally located at B . Under this condition $l = z_1 + z_2$ which equals the distance between knife-edges. Or both knife-edges are fixed and the movable masses of the pendulum are adjusted until the above condition is realized. This is signalized by an equality in the period taken from either knife-edge. Let us suppose, however, that in the adjustment the knife-edges fall at B and D respectively. It is evident that the distance between knife-edges is no longer the equivalent length of the pendulum, being now too short; similarly, if the knife-edges fall at A and E the distance between knife-edges is too great. Under these conditions the relation between the distance (L) between knife-edges and the equivalent length (l) is given by the equation

$$L = l \pm \sqrt{l^2 - 4a^2}. \quad (6)$$

A special case arises when $l = 2a$ and $L = l$; under this condition it is seen from (3) that $z_1 = z_2$ and that the centroid is located mid-way between the knife-edges. The further condition is involved that $a = \frac{1}{2}L$. Graphically this condition is expressed in Fig. 1 by the coalescence of the two circles. It is thus seen that it is pos-

sible (contrary to the general statements found in text-books) to have the centroid midway between the knife-edges and yet to bring the pendulum into adjustment.

The Equation of the Pendulum. — Let Fig. 2 represent a reversible pendulum having fixed knife-edges k_1 and k_2 , and a movable mass m , all other parts being fixed.

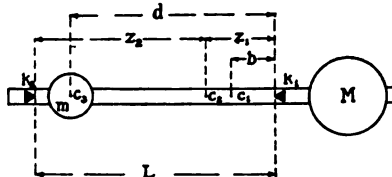


Fig. 2.

Let M = the mass of the pendulum aside from m ,
 b = the distance from k_1 to C_1 , the centroid of M ,
 z_1 = the distance from k_1 to C_2 , the centroid of $M + m$,
 z_2 = the distance from k_2 to C_2 , the centroid of $M + m$,
 d = the distance from k_1 to C_3 the centroid of m ,
 $I_b = Ma^2$ = the moment of inertia of M about C_1 ,
 $I = (M + m)a^2$ = the moment of inertia of $M + m$ about C_2 ,
 $I_m = m\beta^2$ = the moment of inertia of m about C_3 ,
 a = the radius of gyration of $M + m$ about C_2 ,
 $R = m/M$,

Then $a^2 = I/(M + m)$; whence from equation (1),
 $l_1 = z_1 + I/z_1(M + m)$. But since $I = I_b + I_m + M(z_1 - b)^2 + m(d - z_1)^2$,

therefore

$$l_1 = z_1 + \frac{I_b + I_m + M(z_1 - b)^2 + m(d - z_1)^2}{z_1(M + m)}; \quad (7)$$

Whence

$$t = \pi \sqrt{\frac{l}{g}} = \pi \left\{ \frac{z_1}{g} + \frac{I_b + I_m + M(z_1 - b)^2 + m(d - z_1)^2}{gz_1(M + m)} \right\}^{\frac{1}{2}}. \quad (8)$$

From the principle of moments, $M(z_1 - b) = m(d - z_1)$, or

$$z_1 = (Mb + md)/(M + m) = \frac{b + Rd}{1 + R}. \quad (9)$$

Squaring both sides of equation (8) and substituting from equation (9) it is seen that,

$$\frac{gt_1^2}{\pi^2} (b + Rd) = Rd^2 + b^2 + a^2 + R\beta^2. \quad (10)$$

In equations (8) and (10) the pendulum is supposed to be suspended from k_1 . If now the pendulum be suspended from k_2 the terms b , z_1 , and d appear as $L - b$, $L - z_1$, and $L - d$, so that equation (10) becomes,

$$\frac{gt_2^2}{\pi^2} [L(1 + R) - (b + Rd)] = R(L - d)^2 + (L - b)^2 + a^2 + R\beta^2. \quad (11)$$

Equations (10) and (11) may be called the equations of the reversible pendulum.

A discussion of these equations constitutes the problem of the reversible pendulum. In this discussion there is a choice of terms that may be taken as variables. The pairs of variables that will be investigated are (1) t and d , (2) t and β , (3) t and R . Inspection shows that b is not independent of d , and that a change in a has essentially the same effect as a change in β , so that the above pairs are sufficient to cover the problem.

DIVISION I. t AND d TAKEN AS VARIABLES.

If in equations (10) and (11) the origin be moved to

$$\left(-\frac{b}{R}, 0\right) \text{ and } \left(\frac{L}{R} - \frac{b}{R} + L, 0\right)$$

respectively, and in (11) d be changed to $-d$, the equations reduce respectively to

$$\left. \begin{aligned} t_1^2 d &= Ad^2 + Bd + C \\ t_2^2 d &= A'd^2 + B'd + C' \end{aligned} \right\} \quad (12)$$

where the constants have the following values:

$$A = \frac{\pi^2}{g}; \quad B = -\frac{2\pi^2 b}{Rg}; \quad C = \frac{\pi^2}{g} \left[\frac{(1 + R)b^2}{R^2} + \frac{a^2}{R} + \beta^2 \right],$$

$$A' = \frac{\pi^2}{g}; \quad B' = \frac{2\pi^2(L - b)}{Rg}; \quad C' = \frac{\pi^2}{g} \left[\frac{(1 + R)(L - b)^2}{R^2} + \frac{a^2}{R} + \beta \right].$$

Applying the criterion suggested by Sir Isaac Newton for cubic curves of the form of equations (12) it is seen that the roots of both $Ad^2 + Bd + C = 0$, and $A'd^2 + B'd + C' = 0$ are imaginary, since

$$B^2 - 4AC = -\frac{4\pi^4}{g^2} \left[\frac{b^2 + a^2}{R} + \beta^2 \right]$$

and

$$B'^2 - 4A'C = -\frac{4\pi^4}{g^2} \left[\frac{(L-b)^2 + a^2}{R} + \beta^2 \right],$$

both of which quantities are necessarily negative. Therefore both (10) and (11) are of the fifty-third species in Newton's classification. The form of this curve is represented in Fig. 3. Since the right-

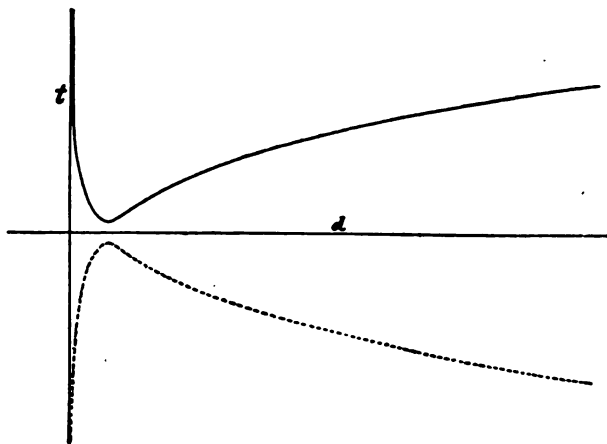


Fig. 3.

hand side of (10) is always positive, t_1 is real for any value of d which makes the left side positive. The condition for real values of t_1 then becomes:

$$d > -\frac{b}{R}. \quad (13)$$

It follows that if b is positive t_1 is real for all positive values of d and for negative values numerically smaller than b/R . If b is negative t_1 is real only when d is positive and numerically greater than b/R . For $d = -b/R$ t_1 is infinite, and the curve has an asymptote parallel to the axis of t at this point. (In Fig. 3 the origin has been shifted so that the Y axis is this asymptote.) In the pendulum a negative value of d means that the centroid of the movable mass is above k_1 , and when it is at a distance b/R above k_1 the centroid of the whole pendulum is at the supporting knife-edge. If

the movable mass be still further above k_1 the pendulum is unstable, a condition indicated by an imaginary value for t_1 in equation (10).

In like manner t_2 in (11) is real for,

$$d < L + (L-b)/R \quad (14)$$

It is easy to see that for the limiting value of d here given the centroid of the whole pendulum is at k_2 . The line $d = L + (L-b)/R$ is an asymptote to the curve, the value of t_2 approaching infinity as d approaches this value.

Differentiating equation (10) and regarding t_1 as the dependent and d the independent variable the expression is obtained :

$$\frac{dt_1}{d(d)} = \frac{R(2\pi^2 d - g t_1^2)}{2g t_1 (Rd + b)}. \quad (15)$$

This is zero when

$$\frac{g t_1^2}{\pi^2} = 2d.$$

Eliminating t_1 between (10) and this equation the values of d for maxima or minima are had. These values are,

$$d = -\frac{b}{R} \pm \sqrt{\frac{b^2}{R^2} + \frac{b^2 + a^2}{R} + \beta^2} \quad (16)$$

The negative value of the radical gives an imaginary value for t_1 since it puts d beyond the limit assigned by (13). Hence there is but one such real point, and it may be shown that this corresponds to a minimum point for positive values, and a maximum for negative values of t_1 . Since we are concerned only with conditions that may be experimentally realized, positive values of t_1 are alone considered.

In a similar manner, by differentiating equation (11) the expression is had :

$$\frac{dt_2}{d(d)} = \frac{R[g t_2^2 - 2\pi^2(L-d)]}{2g t_2 [R(L-d) - (L-b)]}. \quad (17)$$

From which we get :

$$d = \frac{L(R+1) - b}{R} \pm \sqrt{\frac{(L-b)^2}{R^2} + \frac{(L-b)^2 + a^2}{R} + \beta^2}, \quad (18)$$

for points of maxima or minima.

The positive value of the radical gives an imaginary value to t_2 since it throws d outside of the limit assigned by (14). The negative value of the radical gives a minimum for positive values of t_2 , and as before it is seen that there is but one such real point.

It is interesting to note that for these minimum points on the two curves the values of t_1 and t_2 are given by the expressions

$$t_1 = \pi \sqrt{\frac{2d}{g}} \quad \text{and} \quad t_2 = \pi \sqrt{\frac{2(L-d)}{g}}, \quad (19)$$

thus showing that at these points the equivalent lengths are respectively equal to $2d$ and $2(L-d)$. If in addition to this we specify that $t_1 = t_2$ then it is seen that $L-d = d$, or $d = \frac{1}{2}L$. This involves the condition that the two curves shall be tangent to each other on the horizontal line

$$t = \pi \sqrt{\frac{L}{g}}.$$

An interesting case arises when $b = \frac{1}{2}L$. Equations (16) and (18) become

$$\left. \begin{aligned} d' &= -\frac{L}{2R} \pm \sqrt{\frac{L^2}{4R^2} + \frac{L^2 + 4a^2}{4R} + \beta^2}, \\ d'' &= L + \frac{L}{2R} \pm \sqrt{\frac{L^2}{4R^2} + \frac{L^2 + 4a^2}{4R} + \beta^2}. \end{aligned} \right\} \quad (20)$$

The negative value of the radical in the upper equation is precluded by equation (13), as is also the positive value in the lower equation by (14). Applying this fact, it will now be seen that $d' + d'' = L$, or in words: *when the centroid of the fixed part of the pendulum is placed midway between the knife-edges then the sum of the abscissas of the minimum points of the two curves equals the distance between the knife-edges.*

Of the nine possible intersections of two cubic curves, in the present case three are imaginary or at infinity, three belong to the condition that t is negative, and three belong to positive values of t , and can hence be experimentally realized.

Subtracting equation (10) from (11) the locus of the line passing through the intersection points is obtained. This gives :

$$\left(L - \frac{gt^2}{\pi^2}\right)[L - 2b + R(L - 2d)] = 0. \quad (21)$$

From this two straight lines are obtained. The first is the line

$$t = \pi \sqrt{\frac{L}{g}}, \quad (22)$$

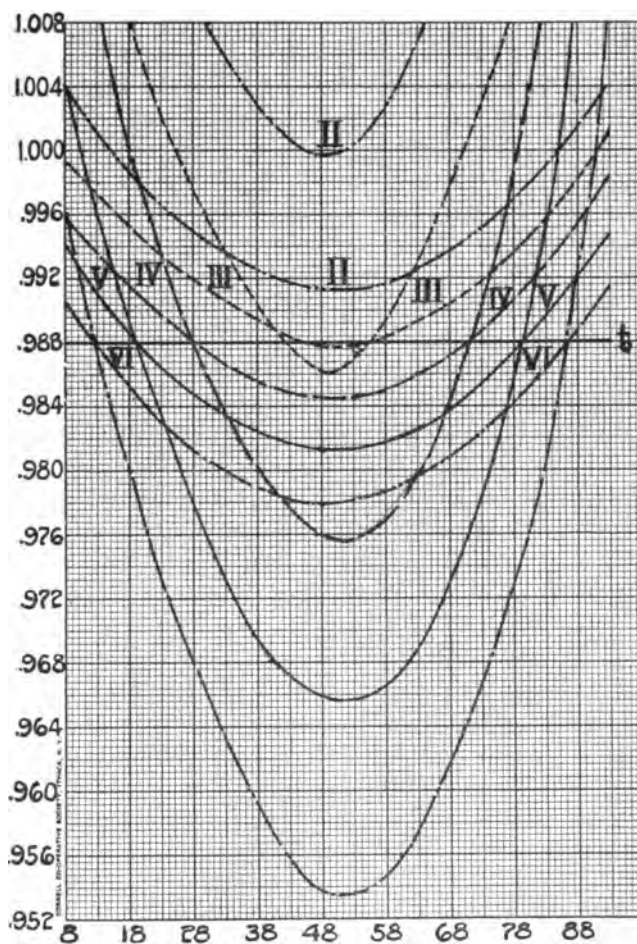


Fig. 4.

and inspection shows that two of the intersections lie on this line which is parallel to the X -axis and at a distance $\pi \sqrt{L/g}$ above it. It is one or other of these intersections (see Fig. 4) that is generally

sought for in experimental work and is the condition used by Kater, *i. e.*, that the equivalent length of the pendulum shall equal L . Eliminating t from equations (10) and (22) the values of the abscissas of the intersection points are had. This gives

$$d = \frac{1}{2}L \pm \sqrt{L^2 - 4 \left[\frac{a^2}{R} + \beta^2 - \frac{b}{R}(L - b) \right]}. \quad (23)$$

This expression shows that the intersection points lie symmetrically with respect to the point midway between k_1 and k_2 . As seen above, the curves became tangent, *i. e.*, the intersection points coincide at the point $(\frac{1}{2}L, \pi\sqrt{L/g})$. Under this condition the radical in (23) is equal to zero and

$$R(\beta^2 - \frac{1}{4}L^2) = b(L - b) - a^2. \quad (24)$$

The second line obtained from (21) is :

$$d = \frac{L(R + 1) - 2b}{2R}. \quad (25)$$

This line is parallel to the axis of Y and passes through the third intersection of the two curves. This third intersection marks the condition when the centroid of the whole pendulum falls midway between k_1 and k_2 . It may fall on either side of the first two intersections or between them. Again, it may coincide with either of them or all three may coincide. Substituting the value of d in (25) into equation (10) the value of t is found to be :

$$t = \left[\frac{\pi^2 (L - 2b + RL)^2 + 4R(b^2 + a^2 + R\beta^2)}{LR(R + 1)} \right]^{\frac{1}{2}}. \quad (26)$$

This is the common period from either knife-edge on the condition that $z_1 = z_2$. Whether this intersection fall below, upon, or above the line

$$t = \pi \sqrt{\frac{L}{g}}$$

depends upon whether

$$\frac{(L - 2b)^2}{R} + \frac{4(a^2 + R\beta^2)}{1 + R}$$

is less than, equal to, or greater than L^2 . The coördinates of the three intersection points are as follows :

$$\begin{aligned}
 (1) \quad & \left\{ \begin{aligned} d_1 &= \frac{1}{2}L + \sqrt{\frac{RL^2 + 4(L-b)b - 4(a^2 + R\beta^2)}{4R}}, \\ t_1 &= \pi \sqrt{\frac{L}{g}}, \end{aligned} \right. \\
 (2) \quad & \left\{ \begin{aligned} d_2 &= \frac{1}{2}L - \sqrt{\frac{RL^2 + 4(L-b)b - 4(a^2 + R\beta^2)}{4R}}, \\ t_2 &= \pi \sqrt{\frac{L}{g}}, \end{aligned} \right. \\
 (3) \quad & \left\{ \begin{aligned} d_3 &= \frac{L(R+1) - 2b}{2R}, \\ t_3 &= \left[\frac{\pi^2 (L - 2b + RL)^2 + 4R(b^2 + a^2 + R\beta^2)}{2g LR(R+1)} \right]^{\frac{1}{2}}. \end{aligned} \right.
 \end{aligned} \tag{27}$$

The conditions required for a coincidence of any two of the points are readily had by assuming the coördinates of 1 and 2, 1 and 3, and 2 and 3 successively equal. This gives three cases with a fourth where all three points coincide.

Case 1. $d_1 = d_2 = \frac{1}{2}L$. — The term under the radical here equals zero. Setting this equal to zero and solving for b the expression is had

$$b = \frac{1}{2}L \pm \sqrt{\frac{1}{4}L^2(R+1) - a^2 - R\beta^2}. \tag{28}$$

These values of b are seen to be symmetrical with respect to the value $d = \frac{1}{2}L$. If $b = \frac{1}{2}L$ then the centroid of the whole pendulum is at this point (since $d = \frac{1}{2}L$) and the three intersections coincide. Keeping the first two interesections together, the third will move to the right or left according as the + or - sign holds good in equation (28).

Cases 2 and 3. — The condition for these cases may be expressed by the equation

$$L = 2b \pm 2R\sqrt{K}$$

where

$$K = \frac{RL^2 + 4(L-b)b - 4(a^2 + R\beta^2)}{4R}.$$

Solving for the value of b we find that

$$b = \frac{1}{2}L \pm \sqrt{\frac{RL(R+1) - 4R(a^2 + R\beta^2)}{R+1}}. \quad (29)$$

The negative sign is to be used for case 2 and the positive sign for case 3. It is here seen that, beginning with the value $b = \frac{1}{2}L$ (when all three intersections coincide) the tangency point recedes to the right (case 3) or left (case 2) as b increases or decreases. It will be noticed that a given change in the variable in equation (29) will produce an equal change in the value of b under both case 2 and case 3. In a sense, therefore, the points of tangency may be said to be symmetrically located with respect to the value $b = \frac{1}{2}L$.

Case 4. — The condition reduces to the condition that $d = \frac{1}{2}L$ and also $b = \frac{1}{2}L$. This gives a value for R , $R = (4a^2 - L^2)/(L^2 - 4\beta^2)$. Since R must be positive, this gives $a \geq L/2 \geq \beta$. If $R = 0$, $L^2 = 4a^2$, a result given by equation (6) if $L = l$. Finally it may be noted that if $b = \frac{1}{2}L$ (but $L - 2b \mp 2R\sqrt{K} \neq 0$) then the third intersection falls on the line $d = \frac{1}{2}L$ but below the line $t = \pi\sqrt{L/g}$.

In the literature of the subject it is generally assumed that the centroid of the pendulum must not be allowed to fall midway between k_1 and k_2 . From the preceding it is seen that this is permissible and that the value of t is then given by equation (26); and, further, that this expression may reduce to the usual one given in equation (22). A glance at equation (26) is sufficient, however, to convince one that this equation cannot be used in practice; also, when the three points of intersection coincide and equation (26) reduces to (22) the curves become osculating curves and the intersection point is not well defined, hence the condition $z_1 = z_2$ is in practice on all accounts to be avoided.

DIVISION II. t AND β TAKEN AS VARIABLES.

In order that a change in β shall not produce a change in d also, the pendulum must be modified as shown in Fig. 5, which represents a pendulum with two knife-edges k_1 and k_2 and with two movable masses m_1 , m_2 which can be so moved along the bar of the pendulum that their centroid (c_3) shall remain fixed. The distance of these masses from c_3 may be called q and it is seen that the moment of inertia of the movable mass becomes $2m\beta_0^2 + 2mq^2$ in

which $m\beta_0^2$ is the moment of inertia of m_1, m_2 , each about its own centroid. Equation (10) may now be written

$$gt^2/\pi^2(b + Rd) = Rq^2 + R\beta_0^2 + Rd^2 + b^2 + a^2. \quad (30)$$

t and q are the variables in this equation and it is therefore of the form

$$At^2 = Bq^2 + C \quad (31)$$

where

$$A = g/\pi^2(b + Rd), \quad B = R, \quad \text{and} \quad C = R(\beta_0^2 + d^2) + b^2 + a^2.$$

The constants A , B , and C are necessarily positive.

Equation (31) is the equation of a central hyperbola whose axis is the axis of Y . Since negative values of t and q are not permissible, that part of the curve falling in the first quadrant is alone to be considered. From equation (31) it appears that t is a minimum for q equals zero, varies in the same sense as C and in the opposite sense as A . The equation of the asymptotes is,

$$t = \pm \frac{B}{A} q = \pm \frac{R\pi^2 q}{g(b + Rd)}, \quad (32)$$

which shows that the slope of the asymptotes varies inversely as

$$\left(\frac{b}{R} + d\right).$$

If the pendulum be swung from the second knife-edge equation (27) becomes :

$$\frac{gt^2}{\pi^2} [L - b + R(L - d)] = Rq^2 + R\beta_0^2 + R(L - d)^2 + (L - b)^2 + a^2 \quad (33)$$

which is of the same form as (28) but with changed values for the constants.

If in equations (27) and (30) y be substituted for t^2 and x for q^2 as the variables, the equations take the form,

$$Ay = Bx + C \quad \text{and} \quad A'y = B'x + C' \quad (34)$$

in which A , B , and C and A' , B' , and C' have the same values as before. Equations (34) are the equations of two straight lines

having different slopes. The intersections of all the pairs of lines represented by (34) lie on the line,

$$y = \frac{C - C'}{A - A'} = \frac{\pi^2 L}{g}. \quad (35)$$

The condition for a realizable intersection is that the coördinates (x_1, y_1) of the point of intersection both be positive. y_1 necessarily is positive, from (35); and substituting this value of y_1 in the equations of (34) shows that x_1 is positive, provided

$$L > (I_b + I_{2m} + Mb^2 + 2md^2)/(Mb + 2md).$$

This condition may be expressed thus: *x is positive when the distance between the knife-edges is greater than the ratio between the moment of inertia of the whole pendulum about the supporting axis, and its moment about the same axis.*

If the slope of the lines of equation (34) be $\tan \varphi_1$ and $\tan \varphi_2$, then

$$\tan \varphi_1 = \frac{\pi^2 R}{g(b + Rd)} = \frac{2\pi^2 m}{gz(M + 2m)},$$

and

$$\tan \varphi_2 = \frac{\pi^2}{g} \frac{R}{L(R + 1) - Rd - b} = \frac{\pi^2}{g} \frac{2m}{(L - z)(M + 2m)}.$$

In order that the intersection of the lines be as well defined as possible, the angle $(\varphi_1 - \varphi_2)$ must be as large as possible. So long as at least one of the angles is small this condition may be stated as $(\tan \varphi_1 - \tan \varphi_2)$ as great as possible. This leads to the expression:

$$\tan \varphi_1 - \tan \varphi_2 = \frac{2\pi^2 m}{g(M + 2m)} \left(\frac{1}{z} - \frac{1}{L - z} \right), \quad (36)$$

This means m large, M small, *i. e.*, R large, z small and L large. Under these conditions (36) practically reduces to

$$\tan \varphi_1 - \tan \varphi_2 = \frac{\pi^2}{g} \times \frac{1}{z}$$

and is therefore inversely proportional to z . Now approximately $z = b/R + d$, and the above condition is seen to be that R shall be

large, b and d small and one of them negative: it being remembered that z must remain finite and positive.

Such a pendulum would consist of a bar as light as rigidity would permit, carrying two knife-edges and having two equal movable masses. Such a pendulum is shown in Fig. 5 and data derived from

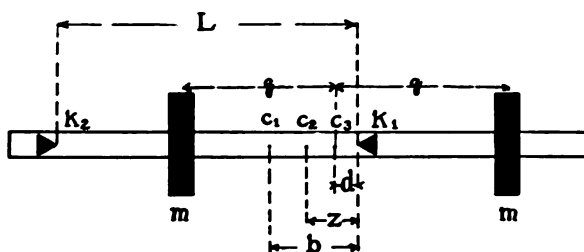


Fig. 5.

it illustrated in Fig. 6. In the lower diagram of this figure the intersection of the two lines is obtained by extrapolation and by using a pendulum so proportioned that it is impossible to bring it into final adjustment. It is a curious fact that if the graphs of the hyperbolæ themselves had been plotted (as in the first division of

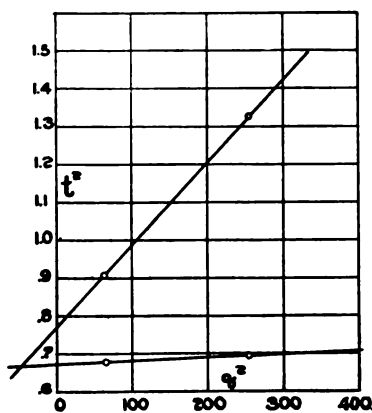


Fig. 6.

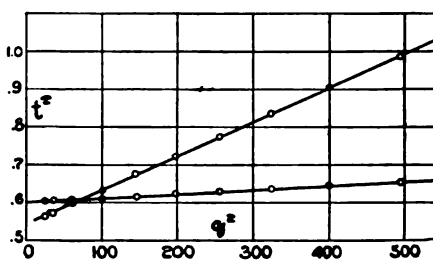


Fig. 6. a.

the paper) no intersection would have been secured. This is evident for the required value of q^2 is negative and q therefore imaginary. The curves would simply approach and recede as do curves

II. in Fig. 4. In spite of this fact the true value of g is gotten from the data, and the point of intersection in Fig. 6 is the means for getting this value.

DIVISION III. t AND R TAKEN AS VARIABLES.

If in equations (10) and (11) t and R be taken as the variables and the origin of (10) be moved to $(-b/d, 0)$ and of (11) to $[-(L-b)(L-d), 0]$ these equations reduce to:

$$\left. \begin{aligned} t_1^2 R' &= AR' + B \\ t_2^2 R' &= A'R' + B' \end{aligned} \right\}, \quad (37)$$

where

$$A = \frac{\pi^2}{g} \frac{d^2 + \beta^2}{d}, \quad B = \frac{\pi^2 b}{g d} \left(\frac{b^2 + a^2}{b} - \frac{d^2 + \beta^2}{d} \right),$$

$$A' = \frac{\pi^2}{g} \frac{(L-d)^2 + \beta^2}{L-d}, \quad B' = \frac{\pi^2 L-b}{g L-d} \left(\frac{(L-b)^2 + a^2}{L-b} - \frac{(L-d)^2 + \beta^2}{L-d} \right).$$

If the constants be positive these equations belong to Newton's sixtieth species of cubics. If B or B' be negative while the coeffi-

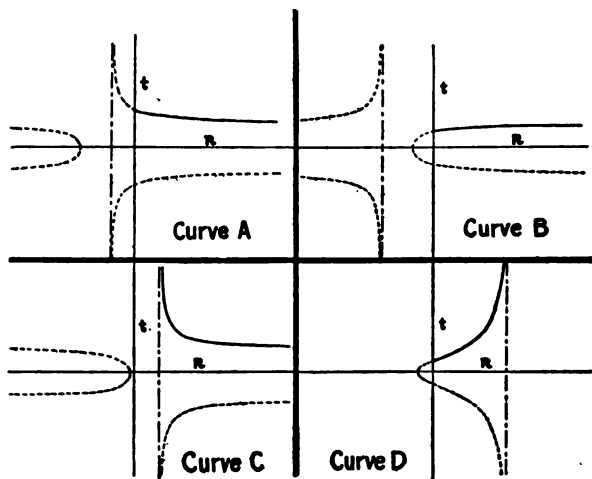


Fig. 7.

cient of R' is positive, changing R' to $-R'$ will have the effect of changing the sign of the absolute term, thus reducing the equa-

tion to the same species as before. If A or A' be negative, the corresponding equation will belong to Newton's sixty-third species, after changing R' to $-R'$ if necessary, to make the absolute term positive

In equation (10) four forms arise (Fig. 7). (A) b and d positive and $(b^2 + \alpha^2)/b > (d^2 + \beta^2)/d$. This makes A and B positive. (B) b and d positive, and $(b^2 + \alpha^2)/b < (d^2 + \beta^2)/d$. This makes A positive and B negative. (C) b negative and d positive. This makes both A and B positive. (D) b positive and d negative. This makes A and B both negative. Case (A) is distinguished from (C) in that the asymptote $R = -b/d$, to equation (10) is on the negative side of the Y -axis in (A) and on the positive side in (C). The values b and d negative, gives two more cases, which, however, do not concern us as no part of the resulting curves lies in the first quadrant. The four cases are illustrated in Fig. 7, where the general shape of the resulting curves is shown. Equation (11) yields a similar number of cases by substituting $L - b$ for b and $L - d$ for d .

Differentiating (10) and (11) with respect to R we obtain,

$$\left. \begin{aligned} \frac{dt}{dR} &= \frac{\pi}{2\sqrt{g}} \frac{(d^2 + \beta^2)b - (b^2 + \alpha^2)d}{(Rd + b)^{\frac{1}{2}} [(d^2 + \beta^2)R + b^2 + \alpha^2]^{\frac{1}{2}}} \\ \frac{dt'}{dR} &= \frac{\pi}{2\sqrt{g}} \frac{[(L-d)^2 + \beta^2](L-b) - [(L-b)^2 + \alpha^2](L-d)}{[R(L-d) + L-b]^{\frac{1}{2}} \{[(L-d)^2 + \beta^2]R + (L-b)^2 + \alpha^2\}^{\frac{1}{2}}} \end{aligned} \right\} (38)$$

The form of these derivatives shows that the curves have on maxima or minima. If b and d are both positive, dt/dR is always positive or always negative according as $(d^2 + \beta^2)/d >$ or $< (b^2 + \alpha^2)/b$. When

$$R = 0, \quad t = \pi \sqrt{\frac{b^2 + \alpha^2}{gb}}.$$

When

$$R = \infty, \quad t = \pi \sqrt{\frac{d^2 + \beta^2}{gd}}.$$

The corresponding conclusions are reached for dt'/dR by putting $L - b$ for b and $L - d$ for d .

Equation (21) gives the lines passing through the intersection points, as in Division II., and the following are the coördinates of the intersections. From the first factor :

$$\left. \begin{aligned} t_1 &= \pm \pi \sqrt{\frac{L}{g}}, \\ R_1 &= -\frac{Lb - (b^2 + \alpha^2)}{Ld - (d^2 + \beta^2)}. \end{aligned} \right\} \quad (39)$$

From the second factor :

$$\left. \begin{aligned} t_2 &= \pm \frac{\pi}{\sqrt{g}} \left[\frac{(L - 2d)(b^2 + \alpha^2) - (L - 2b)(d^2 + \beta^2)}{L(b - d)} \right]^{\frac{1}{2}} \\ R_2 &= -\frac{L - 2b}{L - 2d}. \end{aligned} \right\} \quad (40)$$

It is here seen that while t is double valued (the + value alone being available) R is single valued in both cases. There are thus but two intersection points that can fall within the first quadrant.

Of course, the condition realized by the first intersection is the one desired, since here equation (22) holds good. To make it possible to obtain this intersection R_1 must be positive, and the following table gives all combinations of the signs of the four quantities b , $L - b$, d , $L - d$, with which it is possible to effect this. To the right of each combination are the necessary accompanying conditions on the constants. It will be found that all other combinations are either mere duplicates formed by interchanging the notation with respect to the knife-edges, or else are impossible because L and R are necessarily positive.

	b	$L - b$	d	$L - d$	
I.	+	+	+	+	$\frac{b^2 + \alpha^2}{b} > L > \frac{d^2 + \beta^2}{d}$
II.	+	+	+	+	$\frac{b^2 + \alpha^2}{b} < L < \frac{d^2 + \beta^2}{d}$
III.	+	+	+	-	$L > \frac{b^2 + \alpha^2}{b}$
IV.	+	-	+	+	$L > \frac{d^2 + \beta^2}{d}$

Combination I. produces curve A (Fig. 7) from both knife-edges ; II. gives curve B from both knife-edges ; III. gives curves B and D from k_1 and k_2 respectively ; IV. gives curve A from k_1 and curve B from k_2 .

Conditions of the second intersection may be realized by any combination provided it is possible by a change in R to throw the centroid of the whole pendulum midway between k_1 and k_2 . Since a tangency point, or conditions approaching it are preferably avoided, it would seem likely that a better defined first intersection would be obtained by rendering the second intersection impossible. This may be secured by adjusting the constants so that R_2 in (40) will be negative. The value of R_2 may be written

$$R_2 = -\frac{(L-b)-b}{(L-d)-d}, \quad (41)$$

a form that shows the symmetrical occurrence of the four determining quantities. In cases I. and II., where these quantities are all positive, in order to have R_2 negative $\frac{1}{2}L$ must be either greater or less than both b and d . If $\frac{1}{2}L$ be less than both, the conditions under case I. give $d > \beta$ and $L-b < a$; if $\frac{1}{2}L$ be greater than both, $b < a$ and $L-d > \beta$, for a positive first intersection. In case II, if $\frac{1}{2}L$ be less than b and d , we have $b > a$ and $L-d < \beta$; if $\frac{1}{2}L$ be greater, then $d < \beta$ and $L-b > a$. In case III. the necessary and sufficient condition for R_1 positive and R_2 negative is

$$2b > L > \frac{b^2 + a^2}{b}.$$

This shows that we must have $b > a$ and consequently $b > \frac{1}{2}L > a$, a simpler condition but not so precise as the preceding. The condition in case IV. is

$$2d > L > \frac{d^2 + \beta^2}{d}$$

from which may be deduced the simpler condition $d > \frac{1}{2}L > \beta$.

If we place the values of R_1 and t_1 from (39) in the expressions for the slopes of the two curves, given in (38) we get

$$\frac{dt_1}{dR_1} = \frac{\pi}{2\sqrt{Lg}} \frac{(a^2 + \beta^2 - Ld)^2}{b(a^2 + \beta^2) - d(b^2 + a^2)}, \quad (42)$$

$$\frac{dt_1'}{dR_1} = \frac{\pi}{2\sqrt{Lg}} \frac{(d^2 + \beta^2 - Ld)^2}{(L-b)[(L-d)^2 + \beta^2] - (L-d)[(L-b)^2 + a^2]}. \quad (43)$$

These expressions will be either both positive or both negative under the conditions we are discussing, hence, in general, to get a good angle of intersection it is well to make one as large, and the other as small, as practicable. To make an approximation we may make the denominator of (42) equal to zero, though in practice it should not exactly equal zero as then the curves break down into straight lines and the point of intersection R_1 becomes indeterminate. Doing this, the denominator of (43) reduces to

$$L[(b-d)(L-b-d) - a^2 + \beta^2].$$

This should be large in order to make (43) small. To attain this we must evidently have the difference between b and d , and also the difference between a and β , large.

The above analysis, while reducing the number of permissible cases to four, does not furnish a sufficient criterion between them.

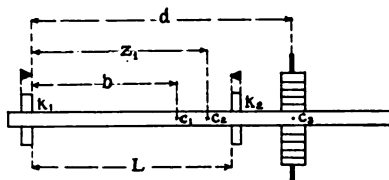


Fig. 8.

It is seen that any of the four may be realized experimentally and it would seem best to leave the question as to which (if any) of the four is to be preferred to be decided by experiment. A design for a pendulum meeting the requirements is given in Fig. 8. R is to be varied by adding thin, circular plates of metal to the cross-piece. It will be noticed that by using this form β is kept constant, as lengthening the cylinder does not alter its radius of gyration about its own axis.

We wish to acknowledge the assistance of Mr. Wm. N. Birchby, particularly in the preparation of the third division. Our thanks are also due to Mr. M. D. Hersey for the preparation of the diagrams.

PHYSICAL LABORATORY,
COLORADO COLLEGE,
December 1, 1906

MEASUREMENT OF ELECTROLYTIC RESISTANCE.

BY *W. S. FRANKLIN AND L. A. FREUDENBERGER.*

THE following methods of measuring electrolytic resistance are based on the use of a transformer, the primary of which is supplied with alternating current and whose secondary consists of a single "turn" of a liquid, the resistance of which is to be measured. The liquid is contained in a glass ring vessel, the ring of glass being formed of two concentric cylinders with the ends ground plane and covered with two flat glass plates. The core of the transformer is built up of 14 mil transformer iron, and it passes through the center of the ring-vessel, so that when the vessel is filled the iron core is surrounded by a closed turn of liquid of regular cross-section.

It was realized early in the work that an alternating current galvanometer was needed, of as great a sensibility as possible, considerably greater than a telephone receiver. For this purpose an alternating current galvanometer was devised by the authors.¹ The galvanometer may be described in brief as an ordinary Kelvin astatic galvanometer in which the suspension is replaced by a suspension consisting of two soft iron magnets inclined 45° to the axis of suspension, and so placed that when the center lines of the magnets are produced they meet in a common point. Such a magnetic system when placed in a uniform vertical alternating field, will be astatic, and by inclining the field slightly from the vertical a directive tendency may be given to the magnet system. If the coils of the Kelvin instrument are now supplied with alternating current of the same frequency as the vertical field, a uni-directional torque acts on the needle.

The first arrangement tried was as shown in Fig. 1.

The two primary coils, P and P' , were connected in series across 110 volts 133 cycle mains; producing, with open secondaries, a

¹ See "A New Type of Alternating Current Galvanometer of High Sensibility," *PHYS. REV.*, Vol. 24, No. 1, Jan., 1907.

magnetic flux in the transformer, as shown by the dotted line. The reluctances of the various legs of the transformer are adjusted so that no flux passes through the test coil, M , which is connected to a telephone receiver or alternating current galvanometer. If now a load is thrown on the transformer by filling the glass vessel with an electrolyte, the balance of magnetomotive forces is disturbed, some flux crosses through the test coil, M , producing sound in the telephone receiver. If the other secondary coil is now closed

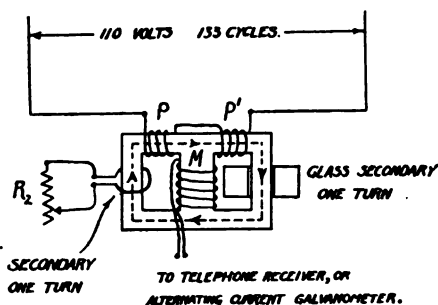


Fig. 1.

through an adjustable resistance, R_2 , a balance of magnetomotive forces may again be obtained, and no sound heard in the telephone receiver; then R_2 is equal to the resistance of the electrolyte in the glass vessel. Of course, the load thrown on the transformer by the single turn of electrolyte is excessively small. It was found, for instance, that when $R_2 = 1$ ohm a deflection of 4 cm. (scale divisions) was produced at the galvanometer, from the zero position of the galvanometer (open-circuited secondaries). The length and cross-section of the electrolytic vessel was such as to make its resistance in ohms equal to the specific resistance of the electrolyte. Thus the presence of the highest conductivity electrolyte could just have been detected. The sensibility of galvanometer was 10^{-6} amperes per centimeter of scale division. $\text{Res.} = 20$ ohms. The galvanometer could not be used for smaller deflections as the zero-point fluctuated through a range of about one centimeter. The amount of flux crossing through the test coil then is extremely small, and, owing to the very low density, the permeability of the iron core through the test core must be extremely low; so low, in fact, as to act as though the iron were nearly a non-magnetic material.

The arrangement shown by Fig. 2 was next tried, in which the coils of the galvanometer were wound differentially.

With open secondaries, and two exactly similar transformers, the slider, *P*, may be adjusted to give zero deflection of the differential galvanometer. The primary coils were connected in series across 30 volt 133 cycle mains. In this, as well as in the first arrangement, the number of turns on the primary coils was such

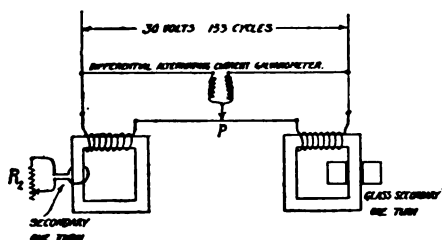


Fig. 2.

as to work the iron to a density of about 1,000 lines per square centimeter. On filling the glass vessel with an electrolyte, the balance on the differential galvanometer is disturbed and may be restored by connecting a resistance, R_2 , across the other secondary coil, equal in value to the resistance of the electrolyte.

With the transformers balanced so as to give zero deflection of the differential galvanometer, with open secondaries, a resistance of 10 ohms (R_2) gave a deflection of 2 centimeters (scale divisions). The sensibility of the differential galvanometer was 10^{-6} amp. per centimeter of scale deflection. Res. of instrument = 1,000 ohms. Some sensibility had to be sacrificed in the galvanometer as it was found necessary to wind the coils of the galvanometer with large clearance between the coils and the suspended magnets; otherwise the differential action of the two windings of the instrument was dependent upon the position of the magnets. The variability of zero was again at least one centimeter of scale deflection.

In both the above methods great difficulty was experienced in properly insulating the coils on the transformers from each other and from the iron core. It was found necessary to insulate with glass. No great attempt was made to attain maximum sensibility in either of the previous methods as they were abandoned in favor

of the following method, shown by Fig. 3, which represents a Wheatstone bridge in which the electrolyte is connected electromagnetically to one of the arms of the bridge.

A slide wire, AB , consisting of 120 feet of No. 16 B. & S. German Silver wire, is wound back and forth on a flat wood surface of convenient size. With secondaries open-circuited the slider, P , is adjusted for zero galvanometer deflection. With the galvanometer

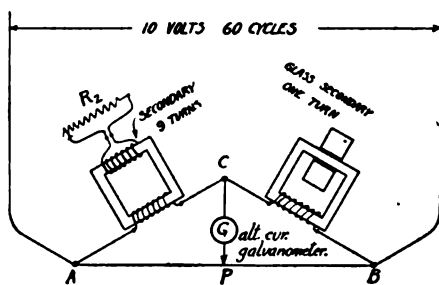


Fig. 3.

used (20 ohms) and a sensibility of 10^{-6} amperes per centimeter of scale deflection, a movement of P of one sixteenth inch in the 120 feet of slide wire caused a galvanometer deflection of 10 centimeters (scale divisions). With a telephone receiver the balance point on the slide wire could only be located within six inches.

The secondary coil actually used consisted of nine turns (instead of one turn) so that the resistance (R_2) necessary to balance the electrolyte of one turn must be divided by 81 (the square of the ratio of turns) to obtain the actual resistance of the electrolyte contained in the glass vessel.

The slider, P , being set so as to give zero galvanometer deflection, 10,000 ohms (R_2) produced a deflection of 2 cm. (scale divisions). The maximum variation of zero, throughout tests was about 1 cm., with an average variation of about .5 cm. A commercial lighting circuit of rather poor regulation was used as the source of current, and the zero of the galvanometer shifted rapidly within the limits specified. With a telephone receiver a resistance of $R_2 = 100$ ohms could just be detected.

The dimensions of the glass ring-vessel were as follows: The inside dimensions of course being given, corresponding to the dimensions of the electrolyte.

Inside diameter	7.83 cm. = r_1
Outside diameter	19.60 " = r_2
Breadth	6.00 " = b .

The above dimensions were obtained by averaging the dimensions around the ring. The dimensions given did not differ more than 0.01 cm. in going around the ring.

The specific conductivity, c , of an electrolyte in reciprocal ohms per centimeter cube is

$$c = \frac{81 \times 1.1413}{R_2}$$

in which R_2 is the balancing resistance shown in Fig. 3 and 1.1413 is the conductivity constant of the given glass cell.

The volume of the electrolytic vessel (by calculation) was 1,521.4 cu. cm. The measured volume (by filling with water) was $1,520 \pm 2$ cu. cm. Owing to the large size of the electrolytic vessel and the regularity of its dimensions, the conductivity constant of the cell can certainly be determined with greater accuracy by calculation from measured dimensions than by measuring its resistance when filled with mercury.

The two primary coils (Fig. 3) were exactly alike and form-wound on glass having 30 turns each; the secondary coil of 9 turns was wound to the same cross-section as the glass vessel; the effective section of iron in each transformer was 17.8 sq. cm., producing a maximum flux density in the iron of about 3,000 lines per sq. cm. Each sheet of 14 mil transformer punching was shellacked and insulated by paper to reduce eddy current losses. By calculation, the magnetizing current of transformer was 1.83 amperes, and the current supplying hysteresis and eddy current losses was 0.178 amp. The no-load current of the transformers thus lags about $84^\circ.5$ behind the impressed e.m.f. in phase. Each transformer may then be considered to consist of a pure reactance of 2.7 ohms in parallel with a pure resistance of 28.0 ohms. When the secondary turn of glass is filled with one of the highest conductivity electrolytes (H_2SO_4 , 30 per cent.) its resistance is about 1 ohm, or reduced to the 30 turn primary it is about 900 ohms. In measuring the resistance of the electrolyte, we are thus measuring the *change* of current produced by connecting a resistance of 900 ohms in parallel

with an impedance of about 2.7 ohms. From the following results it may be seen that this small change of current has been measured with an accuracy of about .5 per cent. for H_2SO_4 . The equivalent resistance and reactance of each primary circuit is not perfectly constant, as small variations are produced in their values due to fluctuations in line e.m.f. and frequency, and also due to temperature differences in each transformer, the zero point of the galvanometer changed continuously in a uniform manner. Since it requires several minutes to fill and empty the glass vessel, the uniform shift of the zero was allowed for by interpolation; keeping current on the transformers for about half an hour until they settled to fairly uniform conditions.

In working the galvanometer the vertical field was brought nearly in phase with the current in the galvanometer (produced by the e.m.f.; *PC*, Fig. 3) by varying the phase position of the current producing the galvanometer field. Any large phase difference (approaching 90°) between the field of galvanometer and the galvanometer current would, of course, considerably reduce the sensibility of the instrument, but would not introduce any errors in the measured resistances.

SAMPLE SET OF OBSERVATIONS.

30 per cent. solution of H_2SO_4 at $19^\circ C$.

		1	2	3	4
I.	$R_2 = \text{infinity.}$	34.8	+ 7.3		28 ^m 30 ^s
	Glass vessel 0.7 full.	27.5			
II.	$R_2 = 120 \text{ ohms.}$	40.9	+17.0	+ 8.9	30 15
	Glass vessel full.	23.9			
III.	$R_2 = 140 \text{ ohms.}$	28.7	- 2.6	+ 9.3	30 45
	Glass vessel full.	31.3			
IV.	$R_2 = \text{infinity.}$	35.0	+10.0		31 30
	Glass vessel 0.7 full.	25.0			
V.	$R_2 = \text{infinity.}$	39.2	+18.2	+10.7	32 15
	Glass vessel empty.	21.0			

Below are given the observations for a low-resistance electrolyte. It was found necessary to make a small correction for eddy currents in the electrolyte. That is, after determining the galvanometer zero with the glass vessel empty; then, on filling to 0.7 full so that the turn of liquid was still broken, the zero point of the galvanom-

eter had shifted. The galvanometer zero at 0.7 full of liquid was used as the reference point, and the correction for eddy currents for the remaining 0.3 volume could then be interpolated. Double deflections were observed by a reversing switch (always thrown in one direction) in the galvanometer circuit.

The numbers given in column I. are the galvanometer readings corresponding to the two positions of the reversing switch in the galvanometer circuit, the numbers in column 2 are the double galvanometer deflections, the numbers in column 3 are the interpolated zero points of the galvanometer based on observations I. and IV., and the numbers in column 4 are the mean clock readings of each pair of galvanometer readings given in column I. The drift from I. to IV. being known, the zero point for II., III., and V. can be interpolated quite accurately, since the drift was found to be very nearly linear with respect to time.

Readings II. and III. serve to determine the value of R_2 (neglecting the effect of eddy currents). That is

(II.) $R_2 = 120$ ohms gives deflection from $+8.9$ to $+17.0 = 8.1$ right.

(III.) $R_2 = 140$ ohms gives deflection from $+9.3$ to $-2.6 = 11.9$ left.

Therefore $R_2 = 128.1$ ohms.

Since R_2 has been determined from galvanometer deflections which include the deflection caused by eddy currents due to 0.7 volume of liquid, it remains, from readings IV. and V., to correct for the eddy currents due to 0.3 volume of liquid. From (IV.) and (V.) it is seen that *emptying* the vessel from 0.7 full produces a deflection from $+10.7$ to $+18.2 = 7.5$ right. *Filling* from 0.7 full would therefore cause a deflection of $0.3/0.7 \times 7.5$ left $= 3.2$ cm. which is equivalent to 6.4 ohms [see (II.) and (III.) above].

This correction, occurring on transformer, *CB* (Fig. 3), means an opposite correction on the other transformer, *AC*. Thus the correction when referred to R_2 is 3.2 cm. *right*, which is equivalent to 6.4 ohms in the direction of lower values of R_2 . Thus the corrected value of R_2 is $128.1 - 6.4 = 121.7$ ohms, and the specific conductivity $= C = 81 \times 1.1413/121.7 = 0.759$ reciprocal ohms per centimeter cube.

The temperature of the electrolyte was measured immediately before filling the glass vessel and immediately after emptying. Temperatures could scarcely have been determined, however, closer than about $0^{\circ}.1$ C. As the temperature correction for $0^{\circ}.1$ C. affects the third place in the specific conductivity, any attempt to secure greater accuracy would necessitate submerging the trans-

TABLE OF RESULTS.

Solution.	Percentage by Weight.	Specific Gravity at 15.5° C.	Temperature Degrees Centigrade.	No. of Observations.	Conductivity in Reciprocal Ohms per Centimeter Cube.	Conductivity (Kohlrausch).	Temperature Coefficient at 18° C.	Temperature Coefficient (Kohlrausch).
KCl.	19.7	1.1327	12.55	3	$0.232 \pm .005$	0.2394	} 0.017	0.0169
			25.38	4	$0.290 \pm .002$	0.2967		
	15	1.1000	12.53	4	$0.184 \pm .007$	0.1822	} 0.015	0.0179
			20.67	5	$0.209 \pm .003$	0.2116		
	10	1.0657	22.50	7	$0.140 \pm .003$	0.1474	} 0.014	0.0200
			12.44	4	$0.074 \pm .005$	0.0643		
	5.25	1.0345	21.50	5	$0.084 \pm .004$	0.0775		
NaCl.	24.6	1.1865	8.36	11	$0.171 \pm .004$	0.1659	} 0.022	0.0226
			18.49	2	$0.212 \pm .001$	0.2121		
			22.25	4	$0.237 \pm .001$	0.2325		
	15	1.1120	13.20	4	$0.141 \pm .008$	0.1475		
KNO ₃ .	9.52	1.0620	15.57	5	$0.082 \pm .004$	0.0762		
NaNO ₃ .	30	1.2277	23.19	5	$0.174 \pm .003$	0.1798		
KOH.	35.7	1.3570	18.10	7	$0.501 \pm .007$	0.5018	} 0.029	0.0283
			21.95	6	$0.558 \pm .012$	0.5495		
	28.56	1.2800	22.00	6	$0.584 \pm .004$	0.5903		
	21.42	1.2060	23.00	6	$0.553 \pm .005$	0.5650		
	14.28	1.1410	21.90	5	$0.445 \pm .004$	0.4383		
	7.14	1.0695	20.50	7	$0.256 \pm .004$	0.2454		
	3.57	1.0340	17.80	5	$0.129 \pm .004$	0.1270		
H ₂ SO ₄ .	95.6	1.8385	17.10	5	$0.108 \pm .006$	0.0963	} 0.013	0.0162
	60	1.4965	19.50	4	$0.402 \pm .004$	0.3846		
	30	1.2200	19.00	4	$0.730 \pm .010$	0.7508		
			28.83	5	$0.820 \pm .025$	0.8684		
	20	1.1420	19.32	4	$0.639 \pm .010$	0.6651		
	10	1.0675	19.81	4	$0.383 \pm .002$	0.4005		
	5	1.0330	19.71	6	$0.216 \pm .007$	0.2128		

NOTE.—In the sixth column (of conductivity), the uncertainty is given as the average deviation from the mean.

former in a thermostat, which would no doubt materially help in reducing the drift of the zero point of the galvanometer, due to unequal temperature changes in the iron of the two transformers.

The foregoing table contains the results of measurements on a number of solutions of salts, bases, and acids of varying percentage strengths. Kohlrausch's values (see "*Das Leitvermogen der Electrolyte*" by Kohlrausch and Holborn, 1898) for the same concentrations and temperatures are given for comparison.

An accurate Wheatstone bridge was used as a rheostat for R_2 (Fig. 3). The bridge was then compared with a new bridge (certified by the Reichsanstalt) and the values of resistances found to be correct within .04 per cent.

An inspection of the above table will show a close agreement, within experimental error, between the results here obtained by the electrodeless ring method and the results of Kohlrausch and Holborn.

The apparatus for the above investigations was constructed under a grant from the Carnegie Institution of Washington, and the experimental work has been done chiefly by the junior author.

NEW BOOKS.

The Theory of Optics. By A. SCHUSTER. London, E. Arnold.

Lehrbuch der Optik. Von PAUL DRUDE. Leipzig, S. Hirzel.

Physical Optics. By R. W. WOOD. New York, The Macmillan Co.

Schuster's Introduction to the Theory of Optics is avowedly influenced by a desire to retain the older philosophical notion of the province of a physical theory. Whether one agrees or not with the author's objection to the "evasive school of philosophy which has received some support from the writings of Heinrich Hertz" it will, in general, be admitted that the treatment is an able one. There is greater continuity of treatment than in some recent works, and because of this, as well as its limitation to topics more frequently discussed in text books, will doubtless commend itself to many for class room use. The discussion of interference, of Talbot's bands and of the nature of white light as well as the chapter on the transmission of energy are worthy of special mention. The biographical notices of those eminent in the development of optics are interesting breaks in the rather rigorous text. For those who incline to a deductive and rather strictly formal treatment this book will be especially pleasing. Many may be more attracted by Wood's comprehensive survey of the experimental field even if the demands of "philosophical" exactness are not so fully met. The book is an admirable example of the printers' art and is remarkably free from typographical errors.

The revised edition of Drude's Optics is of special interest as the last work of this brilliant physicist whose untimely death is mourned by the entire physical world. The revision contains some considerable extensions of the electron hypotheses to the explanation of dispersion, magneto-optics and to radiation. A very clear resumé of Planck's radiation formulæ and their consequences is given and several new references are added in various parts of the work. Had Drude given to science nothing besides this text book with its numerous examples of his genius both as an experimenter and a mathematician his place would have been firmly fixed among the world's truly great physicists.

For clearness and breadth, for depth and suggestiveness, for balance between experiment and theory, this text may well stand as a monument to one of the greatest of modern scientists. Surely all English speaking men of science will gladly join in the wish expressed so well by his assistant Dr. Kiebitz. Möge diesem Buch aussen seinem wissenschaftlichen

Inhalt auch Drude's glückliche Art, wissenschaftliche Probleme aufzufassen und zu behandeln, bleibenden Wert verliehen, und möge es jeden Leser etwas von dem Geiste empfinden lassen, der ihn zu seiner Lehr-tätigkeit begeistert hat, der ihn den Giffel wissenschaftlichen Forschers und Erkennens in der Veredelung der Lebensauffassung und Lebens-führung erblicken liess.

In Wood's Physical Optics we have the emphasis placed on the experimental side of the subject. It would be difficult to collect a more instructive and interesting group of experiments in optics than that presented. The strictly mathematical portions of the book strikes one as somewhat disconnected and resembles a collection of rather carefully selected notes on the subject rather than a formal development. Not that such a treatment is undesirable but that it is in decided contrast with Schuster's or Drude's presentation. The present problems in physical optics are very clearly indicated and many extensions of our knowledge are suggested. Many interesting explanations of rather complicated solar phenomena are given. The work is marred somewhat by occasional errors and misprints. For example, on p. 165, Fig. 141, the axial figures should each have one dimension twice the size of those not on the axis [an error quite common in text books]. On page 117, $x = (\mu - 1)\epsilon a/5$, s should replace the 5. In quite a number of places the notation does not agree with the figures. Apart from these slight defects the book is an inspiration to students and teachers and will be a great aid in rescuing physical optics from the absurd mathematical symbolism which sometimes seems to throttle progress in this fruitful field of investigation.

With these three valuable books at disposal we are better provided with introductions to optical theory than to most other branches of physics.

J. S. SHEARER.

THE PHYSICAL REVIEW.

THE DISCHARGE OF ELECTRICITY FROM POINTED CONDUCTORS DIFFERING IN SIZE.

BY JOHN ZELENY.

I. The discharge of electricity from a pointed conductor is dependent in a large measure upon the shape and size of the point used. In the investigation to be described a study is made of the effect of these qualities upon the current flowing to a plate from a variety of charged points. Incidentally, the effect of moderate changes of pressure and temperature upon the discharge is also considered.

To enable experimental results to be compared with any proposed mathematical analysis of the mechanism of the discharge from points, it is essential that these results be obtained under conditions that can be completely stated and so permit of exact duplication. Such is not the case with the results of previous experimenters on this subject, because the shapes and sizes of the points used are not given, and in some cases the effects are complicated by the presence of insulators and by the special form of the apparatus used.

Chattock,¹ however, found the electric force necessary to start a discharge by measuring the pull on the ends of steel needles having hemispherical ends of different diameters, the needles being connected to earth and placed at various distances from a charged plate. The electric intensity for any point was found to be independent of the distance between the plate and the point, and within certain limits the product of the force by the eight tenths power of the radius of the points was a constant.

¹ Phil. Mag. (5), 32, p. 285, 1891.

Precht¹ measured the potentials required to start a discharge from various sized points when these were directed towards the ceiling of the room, but he found no relation between the potentials and the size of the points.

2. In the experiments to be described in this paper the points used were cylinders of various diameters with their ends either hemispherical or plane. Such points are sufficiently described by simply stating the diameter of the cylinder, and they can be easily duplicated.

The arrangement of the apparatus was such as to give the most simple conditions possible for a point opposite a plane.

The potential required to start a discharge as well as the currents obtained with different potentials was measured in each case.

The subject matter will be treated under the following subdivisions :

(a) Description of apparatus	§ 3
(b) Tests of apparatus	§ 4
(c) Difficulties and irregularities	§§ 5, 6
(d) Procedure in experiments	§ 7
(e) Positive discharge from points with hemispherical ends. Distance = 1.5 cm.	§§ 8, 9
(f) Relation between current, voltage, minimum potential, and diameter of points	§§ 10, 11
(g) Positive discharge from points with hemispherical ends. Distance = 1.0 cm.	§§ 12, 13
(h) Positive discharge from points with plane ends. Distance = 1.5 cm.	§§ 14, 15, 16
(i) Negative discharge	§§ 17, 18, 19
(j) Variation of discharge with pressure	§ 20
(k) Variation of discharge with temperature	§ 21
(l) General remarks	§ 22
(m) Summary	§ 23

DESCRIPTION OF APPARATUS.

3. Since the discharge from points is affected by moisture in the air, it is necessary to place the point and plane in a closed vessel,

¹ Wied. Annal., 49, p. 166, 1893.

to permit the use of dry air. Attempts to use glass vessels of diameters up to 12 cm. proved unsatisfactory¹ because the results obtained with them were not the same as in the open air. Since the current is altered by touching the glass vessel during the discharge, it appears that the glass surface becomes charged sufficiently to affect the potential gradient between the point and plane.

The apparatus finally adopted is shown in diagram in Fig. 1.

The point and plane were inclosed in the brass cylindrical vessel *R*, which was 15 cm. high and 13 cm. in diameter. The plane was a flat, polished, brass disc *O*, 7.5 cm. in diameter. It was supported by the hard rubber post *P*, and the current flowing to it was conducted by means of the rod *Q* and its attached wires to the D'Arsonval galvanometer *G* and its shunt *S*, whence it passed through the telephone receiver *T* to earth.

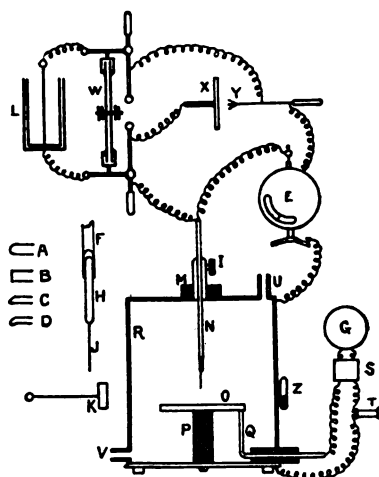


Fig. 1.

The brass rod *N* which carried the points was movable in a metal sleeve, to which it could be fastened by means of the screw *I*. It was insulated from the vessel by the large sulphur plug *M*. The manner in which the points were supported so as to be readily interchangeable, is shown enlarged by *JHF*.

The points *J* were cylindrical wires, for the most part of brass. They were about 1.5 cm. long and were soldered to the holders *H* which were about 3 mm. in diameter. These holders could easily be slipped into the opening *F* at the end of the rod *N*, and were held there by friction.

There was an opening, with a removable cover, in the side of the vessel *R*, which is not shown in the figure. Through this the distance between the point and the plane was adjusted by the aid of the gauge *K*, which consisted of a brass cylinder of a definite

¹ Compare F. Tamm, *Annal. der Phys.* (4), 6, p. 269, 1901.

height carrying a small handle. Placing this gauge on the plate O , the height of the point was brought accurately to the level of the top of the gauge and then clamped in place by the screw I .

The electricity was supplied to the points by a small Wimshurst machine W which was run by a motor. A battery of nine large Leyden jars, represented by L , was placed in parallel with the poles of the machine. This served to maintain a very constant voltage as any irregularities in the generation of electricity by the machine had a negligible effect upon the large capacity of the system. The magnitude of the voltage obtained was regulated by changing the speed of the motor and by altering the distance between the auxiliary point and plane XY , of which the point was always kept negative. For small currents with voltages below 2,000 it was sometimes found necessary simply to turn the machine very slowly by hand.

The potentials were measured by the Braun voltmeter E , reading to 10,000 volts. This was tested by comparing it with a Kelvin vertical electrostatic voltmeter having a range from 500 to 4,000 volts, which was in turn calibrated up to 1,000 volts by means of a battery of storage cells whose potential was determined in steps with an accurate Weston voltmeter.

To avoid any deterioration in the gas with use, a slow stream of air was kept continually flowing through the apparatus by means of a suction pump attached to the opening V . Before entering the apparatus at U the air was dried by passing through a tower of calcium chloride. A long tube filled with cotton was also interposed near U for the removal of dust.

TESTS OF APPARATUS.

4. As it is desirable that the apparatus should give results which approximate to what would be obtained with a very long point opposite an infinite plane, and should be as far as possible independent of the presence of the enclosure, some experiments were carried out to see how far these conditions were fulfilled.

In the first place it was found that the plate used was sufficiently large to satisfy the condition named. With a point at a distance of 1.5 cm. from the plate in the open air, the current obtained with a

given potential was the same as when a plate of twice its diameter was substituted.

The next experiment performed was to determine whether the length of the wire points used (1.5 cm.), attached as they were to the long rod *N*, was sufficient to give the same results as if they were infinitely long. Two points of the same diameter (.26 mm.) and 1.5 cm. and 5 cm. long respectively, were tried in succession in the apparatus at a distance of 1.5 cm. from the plate and the results obtained were again identical. It is not possible to use fine points longer than 1.5 cm. as they are set into vibration by the discharge.

The influence of the cylindrical vessel upon the results was determined by taking readings with a point (.19 mm. in diam.) at different distances from the plate, first with the plate in the open air and next with the plate inside the vessel, undried air being used.

The following results were obtained.

Distance of Point from Plane.	Voltage of Point.	Current in Vessel.	Current in Open Air.
1.0 cm.	6,000 volts.	65.0 divs.	64.5 divs.
1.5	7,500	70.5	68.0
2.0	8,500	71.5	68.2
2.5	9,000	59.5	62.0
3.14	9,500	47.5	54.5

The results indicate that contrary to what might be expected the effect of the vessel is to increase the current when the point is near to the plate, the increase being about 1 per cent. for a distance of 1 cm. and about 3.5 per cent. for a distance of 1.5 cm. At the larger distances the presence of the vessel diminished the current obtained by the plate.

We may account for the increase of current at short distances by considering the effect that the surrounding cylinder has of spreading the lines of force as they approach the plate. This enables a larger total current to flow and, roughly speaking, as long as the area to which the ions go does not extend beyond the limits of the plate the current received by it is increased.

DIFFICULTIES AND IRREGULARITIES.

5. There is a disadvantage in having a short distance between the point and the plane in that it is more difficult to get a steady and

pure point discharge. This rarely caused trouble with the positive discharge, but with the negative discharge it was often impossible to get a steady discharge at all with certain points, especially those of a large diameter. Usually the current was more apt to become intermittent at its higher values, but the opposite was sometimes true that a current unsteady at first became uniform as it was increased.

To test the steadiness or intermittence of the current, the telephone receiver *T* was put into the galvanometer circuit. The intermittence is often due to the superposition of an intermittent effect upon the steady point discharge. Sometimes this constitutes such a small part of the whole current as not to affect the results appreciably. Clicks are heard in the telephone at intervals of a second or more, little specks of light appearing on the surface of the point as if little disruptive discharges were taking place. In such cases, as the current is increased the clicks increase in frequency until the current due to this cause becomes at least a considerable part of the whole. The pitch of the sound heard in the telephone increases with the current and becomes at times so high that it is a question whether sometimes the intermittence may not be so rapid that the telephone and the ear fail to detect it.

The luminous aspect of the discharge, too, serves to determine its nature, since when the light is not confined to the neighborhood of the point itself the discharge is no longer a pure point discharge.¹

6. The potential at which the discharge from some points begins is different from that at which the current ceases, and the discharge shows other irregularities for small currents. This is especially true for the negative discharge. By exposing such points to certain radiations, Gorton and Warburg² found that the potentials at which the current begins and ends become the same. During all of the experiments to be described a glass tube (*Z*, Fig. 1) containing 1 gram of 1 per cent. radium bromide was placed at the side of the vessel *R*. The presence of this tube had no effect upon the larger currents from the points, but it served to make the discharge begin more regularly in the cases referred to above.

¹ J. Stark, *Verh. der Deutsch. Phys. Gesell.*, VI., p. 115.

² Gorton and Warburg, *Annal. der Physik*, 18, p. 128, 1905.

The positive discharge was found on the whole very regular and steady for the large variety of points. As the voltage was increased the current started gradually from zero value (at least the initial current was less than 2×10^{-9} amp.), and at any one voltage underwent but slight variations. When a series of readings for the current was taken with increasing voltages and then repeated with decreasing voltages the values obtained were found to be practically identical, and the potential at which the current ceased was the same as that at which it began.

In the case of the negative discharge, however, the current was apt for certain points to begin with little jerks and to undergo some fluctuations, more especially at its lowest values. On reducing the voltage after the current had been running for some time, the values of the currents obtained were apt to be less than the corresponding ones found before. For most of the points, after they had been used, the current would stop and only begin again at a somewhat higher voltage than was necessary to start it in the first place.

PROCEDURE IN EXPERIMENTS.

7. After a new point had been adjusted in the apparatus and the vessel closed, a stream of dry air was drawn through for some time before the taking of readings was begun. The minimum potential necessary to start a current was then determined first of all, and after this the values of the current were obtained for increasing voltages up to the limit of supply of the machine. Then a smaller number of readings was usually taken with decreasing voltages.

When the voltage for the initial current was determined the sensibility of the galvanometer was 10^{-8} amp. per division on the scale, while for most of the other readings the sensibility was reduced to one tenth of that value.

The potentials for which the currents from the points were determined were usually adjusted so as to have the reading of the voltmeter come exactly on one of its subdivision marks, as this permitted a more exact determination.

Inasmuch as the discharge from points is dependent upon the pressure and temperature of the air, it was necessary to find the magnitude of the variation due to these causes in order to be able

to reduce the different observations to a common condition. The manner in which these corrections were obtained is given in § 20 and § 21. The readings actually taken are given in the tables in each case, but in plotting the results they are all reduced to a pressure of 74 cm. of mercury and a temperature of 22° C., as these values are near to the mean conditions prevailing during the experiments.

POSITIVE DISCHARGE FROM POINTS WITH HEMISPHERICAL ENDS.

DISTANCE = 1.5 CM.

8. The readings obtained for the positive discharge from cylindrical points of different diameters, with hemispherical ends (see *A*, Fig. 1) at a distance of 1.5 cm. from the plate, are given in Table I.

TABLE I.

Positive Discharge from Cylindrical Points with Hemispherical Ends. Distance from Plate = 1.5 cm.

Point Number.	1	2	3	4	5	6	7	8	9
Diameter in mm.	.0244	.039	.091	.174	.244	.50	.73	1.13	2.005
Pressure in cm.	73.0	74.9	74.1	74.1	74.1	74.1	74.1	73.7	73.2
Temperature in °C.	19	21.5	26.5	27.0	27.0	27.0	25.7	26.5	25.5
Starting potential.	1,600	2,000	2,450	3,015	3,365	4,600	5,500	6,700	9,150
Potentials in Volts, with Corresponding Currents in 10 ⁻⁷ Amperes.	1,750	3,000	2,500	3,255	3,500	5,000	5,800	7,000	9,250
	.28	7.2	.5	2.2	1.1	4.8	4.4	6.1	3.3
	2,000	4,000	3,000	3,500	4,000	6,000	6,000	8,000	9,500
	1.5	20.5	4.5	4.5	6.3	22.5	9.3	26.6	12.8
	2,500	5,000	4,000	4,000	5,000	7,000	7,000	9,000	9,750
	5.2	37.2	16.9	10.7	20.8	44.0	28.7	57.7	21.1
	3,000	6,000	5,000	5,000	6,000	8,000	8,000	10,000	10,000
	9.6	62.2	33.8	25.4	41.7	69.9	52.0	99.9	30.0
	4,000	7,000	6,000	6,000	7,000	9,000	9,000		10,500
	23.7	90.2	56.6	46.8	65.9	108.7	88.4		46.6
	5,000	8,000	7,000	7,000	8,000		10,000		
	42.9	124.3	85.1	73.2	95.2		131.2		
	6,000		8,000	8,000					
	68.9		117.2	102.0					
	7,000		8,500	8,700					
	100.6		139.7	131.8					
	8,000								
	135.6								

The table includes the results that were obtained under the conditions given with all of the points used. In cases where readings were repeated the average value is given.

All of the points except nos. 1 and 2 were made of brass wires, the ends being made round on a lathe for the larger points and by careful grinding on a stone for the smaller points. These last appeared quite round under the microscope, except no. 3 which was rather imperfect being too fine to work, properly. Point no. 2 was made

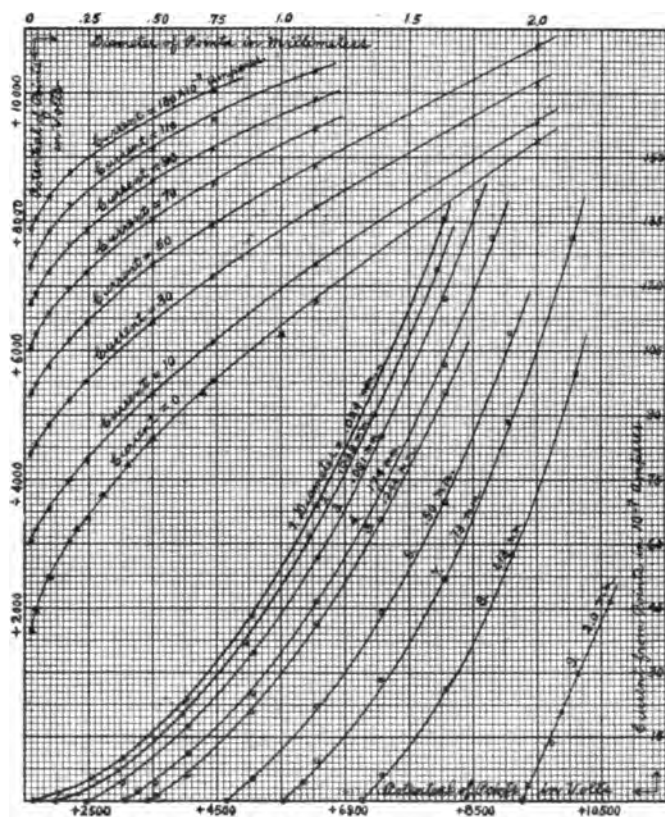


Fig. 2. Positive discharge in dry air from cylindrical points with hemispherical ends. Distance from plate = 1.5 cm. Pressure = 74 cm. Temperature = 22° C.

from a fine platinum wire, and point no. 1 was made from a silver covered platinum wire, the silver being completely dissolved from the end for a distance of 3 mm. The general appearance of the ends of these wires is shown by *C* and *D* respectively in Fig. 1.

9. The results, reduced to a pressure of 74 cm. and a temperature of 22° C. are shown graphically in the lower part of Fig. 2.

The regularity of the results is noted from the good agreement of the different points with their respective curves. It is not directly apparent, however, whether there is any regular relation between the results obtained for the different points and the diameters of these points. To show this, the system of curves in the upper part of the figure was drawn. Here each curve represents the relation between the size of the points and the voltage required to produce a current of the magnitude stated. The values for current = 0 are evidently the starting potentials. The regularity of the results is remarkable for observations of this character, and proves that no irregularities due to surface or other conditions enter into the experiments to a sufficient amount to overshadow the effect of the size of the points. Because of this regular relation it is now possible to use these curves for constructing the potential current curve for a point of any size by plotting the potentials corresponding, for the size in question, to the different currents given. Furthermore, by using such a curve it is quite possible to adopt a point and plane of the character here described, for measuring high potentials with a fair accuracy by simply noting the current flowing to the plate. Corrections for differences of pressure and temperature can be made in the manner given in §§ 20 and 21.

RELATION BETWEEN CURRENT, VOLTAGE, MINIMUM POTENTIAL, AND DIAMETER OF POINTS.

10. The results obtained with points differing so much in size give a severe test to any formula that may be proposed for the relation between the current and potential in point discharge. Several such formulæ have already been applied to different cases of point discharge.¹ Of these, Warburg's formula, $C = aV(V - M)$, best represents the above results for points of all sizes and currents of all values. In this formula, C is the current corresponding to a voltage V , M is the minimum potential required to start a current, and " a " is a constant depending upon the nature of the point and the

¹ E. Warburg, *Wied. Annal.*, 67, p. 72, 1899. H. Sieveking, *Annal. der Physik*, 1, p. 303, 1900. F. Tamm, *Annal. der Physik*, 6, p. 259, 1901. P. Ewers, *Annal. der Physik*, 17, p. 781, 1905.

arrangement of the apparatus. It is apparent from the change in the slope of the curves in Fig. 2 that this constant " a " increases as the diameter of the point increases, and it was found that this increase is very nearly a linear one. For this reason it is possible to represent the whole system of curves by one formula involving the diameter of the points. The formula obtained from the above results for the discharge current in amperes under the conditions named is,

$$C = 2.58 \times 10^{-13} (1 + .110d) V(V-M),$$

d being the diameter of the point in millimeters.

In Table II. a comparison is made of some currents calculated by this formula, with the observed values taken from the potential current curves.

TABLE II.

Comparison of Observed Currents with those Calculated by the Formula
 $C = 2.58 \times 10^{-13} (1 + .110d) V(V-M).$

Diameter of Point.	.024	.039	.091	.174	.244	.50	.73	1.13	2.00
M.	1,620	1,980	2,470	3,050	3,400	4,650	5,530	6,770	9,250
V.	2,500	2,500	3,000	3,500	4,000	5,000	6,000	7,000	9,500
C. calc.	5.7	3.4	4.1	4.1	6.3	4.8	7.8	4.6	7.5
observ.	5.0	3.3	4.3	4.6	6.2	4.9	7.9	3.6	8.1
V.	3,000	3,000	3,500	4,000	4,500	5,500	6,500	7,500	10,000
C. calc.	10.8	7.9	9.4	10.0	13.1	12.7	17.6	15.8	23.6
observ.	9.9	7.7	9.5	10.1	12.5	12.7	16.8	13.0	25.3
V.	4,000	4,000	4,500	4,500	5,000	6,000	7,000	8,000	10,500
C. calc.	24.6	20.9	23.8	17.2	21.2	22.1	28.7	28.6	41.3
observ.	23.6	20.7	24.3	17.0	20.4	21.9	27.2	24.6	42.0
V.	5,000	5,000	5,500	5,500	6,000	7,000	8,000	8,500	
C. calc.	43.8	39.1	43.4	35.3	41.4	46.0	54.4	42.7	
observ.	42.8	38.9	43.9	34.7	40.3	42.1	52.7	38.3	
V.	6,000	6,000	6,500	6,500	7,000	8,000	9,000	9,000	
C. calc.	68.0	62.4	68.3	59.0	66.6	73.1	87.3	58.2	
observ.	68.0	62.7	68.7	57.0	64.4	68.7	85.7	54.3	
V.	7,000	7,000	7,500	7,500	8,000	9,000	10,000	10,000	
C. calc.	97.6	91.0	98.2	88.1	97.4	106.6	124.5	93.6	
observ.	99.6	93.4	98.7	84.7	93.7	105.0	129.3	94.3	
V.	8,000	8,000	8,500	8,500					
C. calc.	132.0	124.8	132.4	122.0					
observ.	134.0	127.2	135.9	119.3					

The agreement while not all that might be desired is nevertheless a fairly good one when everything is considered. It must be noted especially that since the current increases more rapidly than the voltage, the largest deviations between the observed and the calculated values of the current are due to but 2 per cent. change of voltage. Still, this difference is larger than the observational errors and either the relation given is only an approximate one or there was enough irregularity about the points or the discharge from them, to produce this difference.

11. The relation between the size of the point and the voltage for which the discharge begins (M in above formula) is a matter of

TABLE III.

Positive Discharge from Cylindrical Points with Hemispherical Ends. Distance from Plate = 1 cm.

Point Number.	1	2	3	4	5	6	7
Diameter in mm.	.039	.091	.174	.244	.50	1.13	2.00
Pressure in cm.	74.9	72.5	72.5	72.5	72.5	72.5	74.8
Temperature in °C.	20.5	24.2	24.2	24.2	24.2	24.2	26.0
Starting Potential.	1,895	2,300	2,850	3,200	4,425	6,350	8,750
Potentials in Volta, with Corresponding Currents in 10 ⁻⁷ Amperes.	2,000	2,500	3,000	3,500	4,500	6,500	9,000
	1.5	1.9	1.9	5.0	1.3	6.1	13.3
	3,000	3,000	4,000	4,000	5,000	7,000	9,250
	12.8	8.3	20.0	14.4	13.3*	22.2	28.9
	4,000	4,000	5,000	5,000	6,000	7,500	9,500
	33.3	28.9	46.6	38.9	44.4*	38.9	45.0
	5,000	5,000	6,000	6,000	7,000	8,000	9,750
	60.5	57.7	83.3	73.3*	83.8*	60.0	59.9
	6,000	6,000	7,000	7,000	8,000	8,500	10,000
	101.0	97.1	127.6	116.6*	132.1*	88.8	76.6
	7,000	7,000			8,300	9,000	10,250
	149.9	128.8			151.0*	119.9	93.3
						9.250	10,500
						138.8	106.0

For the values marked by a star, the current showed some intermittence.

considerable interest. No simple relation was found to hold well for the whole series of points.

Nevertheless up to a diameter of .7 mm., the values of M when

diminished by a constant number were found to be quite closely proportional to the square roots of the diameters of the points. This relation is given numerically for the above case by the formula, $M = 5,465 \sqrt{d} + 755$, d being the diameter of the point in millimeters. This indicates that with an infinitely fine wire it would still require a potential of 755 volts to start the positive discharge to a plate 1.5 cm. distant. Some values obtained from the above formula have been plotted as triangles on the curve for $C = 0$ in Fig. 2, and it is seen that there is a good agreement with the observed values up to the limit stated.

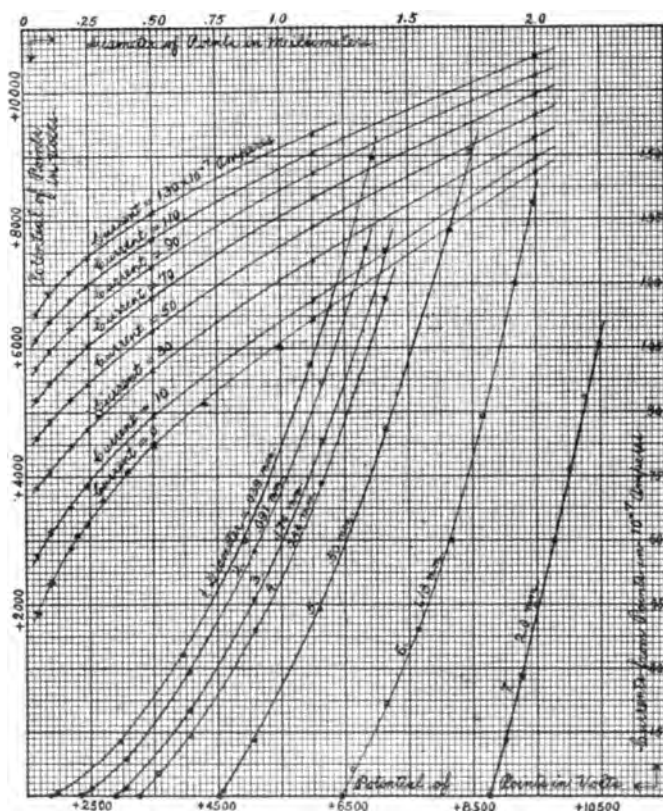


Fig. 3. Positive discharge in dry air from cylindrical points with hemispherical ends. Distance from plate = 1. cm. Pressure = 74 cm. Temperature = 22° C.

Above a diameter of .5 mm. the observed values for M are strictly proportional to the square roots of the diameters of the points and may be calculated by means of the formula, $M = 6,420 \sqrt{d}$.

POSITIVE DISCHARGE FROM POINTS WITH HEMISPHERICAL ENDS.

DISTANCE = 1 CM.

12. The results obtained for the positive discharge from cylindrical points having hemispherical ends when placed at a distance of 1 cm. from the plate, are given in Table III. The points used were the same as the ones of corresponding size in Table I.

TABLE IV.

Comparison of Observed Currents with those Calculated by the Formula
 $C = 4.05 \times 10^{-13} (1 + .235d) V(V - M).$

Diameter of Point.	.099	.091	.174	.244	.50	1.13	2.00
M.	1,870	2,320	2,900	3,250	4,500	6,450	8,730
V.	2,500	3,000	3,500	3,500	5,000	7,000	9,000
C. calc.	6.4	8.4	8.8	3.8	11.3	16.5	14.5
observ.	6.3	8.3	9.4	3.8	11.6	17.3	14.3
V.	3,500	4,000	4,000	4,000	5,500	7,500	9,500
C. calc.	23.2	27.8	18.5	12.8	24.9	40.7	43.5
observ.	22.3	27.4	19.1	12.9	25.6	34.9	43.6
V.	4,000	4,500	4,500	4,500	6,000	8,000	10,000
C. calc.	34.7	40.6	30.3	24.0	40.8	64.0	75.5
observ.	33.7	40.0	30.8	23.7	41.0	54.6	75.0
V.	4,500	5,000	5,000	5,000	6,500	8,500	10,500
C. calc.	48.3	55.4	44.2	37.5	58.9	89.5	110.5
observ.	47.0	54.6	44.8	37.3	58.7	79.7	108.0
V.	5,000	5,500	5,500	5,500	7,000	9,000	
C. calc.	63.9	72.4	60.2	52.9	79.2	118.0	
observ.	63.3	71.5	60.2	52.3	79.3	108.2	
V.	5,500	6,000	6,000	6,000	7,500	9,500	
C. calc.	81.6	91.4	78.1	70.6	102.0	148.5	
observ.	81.7	91.3	78.3	69.9	101.4	142.5	
V.	6,000	6,500	6,500	6,500	8,000		
C. calc.	101.1	112.3	98.5	90.5	127.0		
observ.	103.5	113.0	98.9	89.9	125.5		
V.	6,500	7,000	7,000	7,000	8,500		
C. calc.	122.8	135.5	120.8	112.5	154.1		
observ.	127.0	136.6	120.7	111.5	153.0		

The results, reduced to a pressure of 74 cm. and a temperature of 22° C., are shown graphically in the lower right hand part of Fig. 3.

The curves in the upper left hand part of the figure again show

the relation between the diameter of the points and the potential required to produce the current given in each case. The same regularity appears in the results as in those above and these curves may here too be used for constructing the potential current curve for a point of any size, when placed at a distance of 1 cm. from the plate.

13. The results shown by the family of potential current curves in Fig. 3 may all be well represented by the formula,

$$C = 4.05 \times 10^{-13}(1 + .235d)V(V - M),$$

as is seen from Table IV. where a comparison is made of the observed and calculated values of the current for various potentials. The

TABLE V.

Positive Discharge from Cylindrical Points with Plane Ends. Distance from Plate = 1.5 cm.

Point Number.	1	2	3	4	5	6	7	8	9
Diameter in mm.	.088	.197	.267	.466	.516	.808	1.17	1.68	2.18
Pressure in cm.	73.7	73.7	73.7	73.0	74.8	73.9	73.9	74.1	74.1
Temperature in °C.	26.5	26.5	25.5	20.7	27.5	23.0	23.0	27.5	27.5
Starting potential.	2,440	3,175	3,550	4,475	4,750	5,750	6,800	8,015	9,050
Potentials in Volts, with Corresponding Currents in 10 ⁻⁷ Amperes.	2,500	3,500	4,000	5,000	5,000	6,000	7,000	8,250	9,250
	.8	2.8	4.4	7.3	4.4	5.0	4.4	8.4	10.7
	3,000	4,000	5,000	6,000	6,000	7,000	8,000	8,500	9,500
	4.4	9.4	19.4	27.0	23.3	26.6	28.9	17.5	21.4
	4,000	5,000	6,000	7,000	7,000	8,000	9,000	9,000	9,750
	17.2	25.0	41.1	50.7	47.2	53.3	65.5	37.7*	31.6
	5,000	6,000	7,000	8,000	8,000	9,000	10,000	9,500	10,000
	34.4	47.7	66.0	79.4	76.6	92.1	113.2	61.4*	42.8
	6,000	7,000	8,000	9,000	9,000	9,750		10,000	10,500
	59.9	74.4	96.6	119.4	117.7	129.3		83.4*	63.2
	7,000	7,725	9,000						
	86.0	95.5	139.9						
	8,000								
	122.2								

calculated values for the point whose diameter is 1.13 mm. are all somewhat high and M would have to be increased by 100 volts to bring the numbers into good agreement with the observed results.

The relation between the minimum potential and the diameter of the points is similar to that found for the points at a distance of 1.5 cm. from the plate. Up to a diameter of .7 mm. the values of M may be quite accurately calculated by the equation, $M = 5,340 \sqrt{d} + 675$. Some values obtained by the use of this formula are plotted as triangles on the curve for $C = 0$, in Fig. 3, and it is seen that they

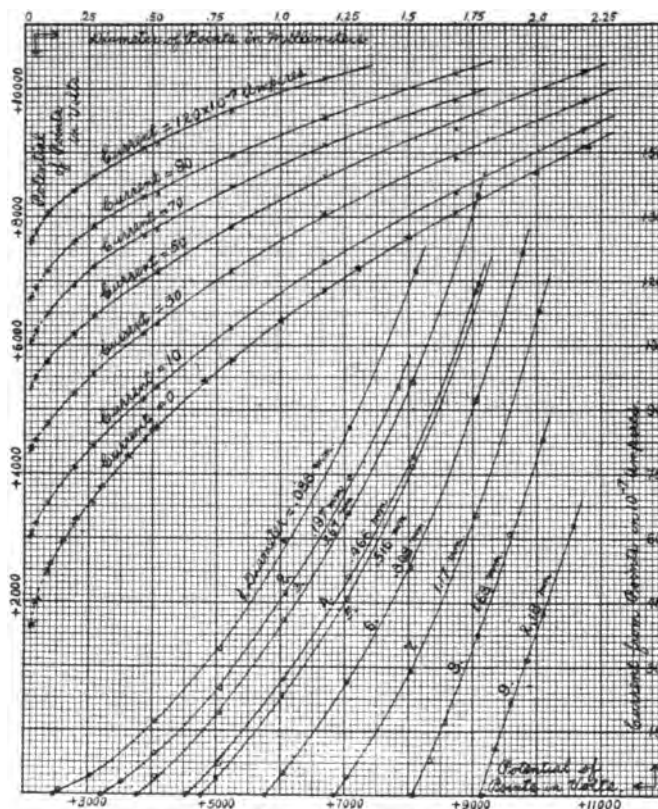


Fig. 4. Positive discharge in dry air from cylindrical points with plane ends. Distance from plate = 1.5 cm. Pressure = 74 cm. Temperature = 22° C.

agree well with the observed values. For diameters larger than .7 mm. the calculated values come out too small and another formula of the same type is necessary to represent the results.

POSITIVE DISCHARGE FROM POINTS WITH PLANE ENDS. DISTANCE
FROM PLATE = 1.5 CM.

14. The results obtained for the positive discharge from cylindrical points with plane ends (see *B*, Fig. 1) are given in Table V. The distance of the points from the plate was 1.5 cm. The points were all made from brass wires.

15. The results, reduced to a pressure of 74 cm. and a temperature of 22° C., are shown graphically in the lower part of Fig. 4.

The relation between the diameter of the points and the potential required to produce any given current is shown for a number of currents by the series of curves in the upper left hand portion of

TABLE VI.

Comparison of Observed Currents with those Calculated by the Formula
 $C = 2.60 \times 10^{-13} (1 + .30d) V (V - M).$

Diameter of Point.	.088	.197	.267	.466	.516	.808	1.17	1.68	2.18
M.	2,460	3,200	3,760	4,510	4,720	5,770	6,830	8,080	9,100
V.	3,000	3,500	4,000	5,000	5,000	6,000	7,000	8,500	9,500
C. calc.	4.3	2.9	2.7	7.3	4.2	4.6	4.0	14.0	16.4
observ.	4.2	2.7	3.3	7.4	4.3	4.3	4.0	14.0	17.5
V.	4,000	4,500	5,000	6,000	6,000	6,500	7,500	9,000	10,000
C. calc.	16.4	16.1	17.4	26.5	23.1	15.8	17.1	32.6	39.7
observ.	16.2	16.0	19.1	26.2	22.8	14.3	15.3	33.8	39.1
V.	5,000	5,000	6,000	6,500	6,500	7,000	8,000	9,500	10,500
C. calc.	33.9	24.7	37.7	38.4	34.8	27.8	31.7	52.6	63.4
observ.	33.9	24.5	39.4	37.1	33.7	26.0	28.8	56.0	60.6
V.	6,000	5,500	7,000	7,000	7,000	7,500	8,500	10,000	
C. calc.	56.7	34.8	63.5	51.6	47.9	42.0	48.2	74.9	
observ.	56.7	34.6	64.4	50.0	46.7	38.8	45.3	79.8	
V.	6,500	6,000	7,500	7,500	7,500	8,000	9,000		
C. calc.	70.1	46.2	78.8	66.3	62.5	57.7	66.2		
observ.	70.0	45.7	78.8	63.7	60.5	53.0	65.4		
V.	7,000	6,500	8,000	8,000	8,000	8,500	9,500		
C. calc.	85.0	59.0	95.1	82.4	78.7	75.1	86.1		
observ.	85.0	58.0	95.4	80.0	76.6	70.6	87.6		
V.	7,500	7,000	8,500	8,500	8,500	9,000	10,000		
C. calc.	100.9	73.1	113.1	100.7	96.5	94.0	107.6		
observ.	101.2	71.5	114.7	97.9	95.1	91.6	110.9		
V.	8,000	7,500	9,000	9,000	9,000	9,500			
C. calc.	118.8	88.6	132.2	119.6	115.6	114.6			
observ.	118.7	86.5	136.2	116.7	115.0	113.3			

the figure. As it is seen that the results for the smallest points are almost identical with those obtained with points having hemispherical ends, as shown in Fig. 2, the values obtained in the latter case for the two fine platinum wires (nos. 1 and 2) are added here and the curves extended through them as broken lines. For the larger points the potential required to produce a given current is smaller for points with plane ends than it is for points with hemispherical ends.

16. The relation between the current and the potential and the size of the points can be represented in this case by the formula,

$$C = 2.60 \times 10^{-12}(1 + .30d)V(V - M),$$

and some values of the current calculated by this formula for various potentials are compared in Table VI. with the observed values taken from the curves in Fig. 4.

The relation between the minimum potential M and the diameter of the points d can in this case be represented throughout the whole range of diameters used by the formula, $M = 5,670\sqrt{d} + 705$. Some values obtained from this formula are plotted as triangles on the curve for $C = 0$ in Fig. 4, and it is seen that they are in good agreement with the observed values.

NEGATIVE DISCHARGE.

17. The results obtained for the negative discharge from cylindrical points with hemispherical ends, at a distance of 1.5 cm. from the plate, are given in Table VII. The points used were the same as those of corresponding size employed for the positive discharge. The currents from the larger points were all intermittent and so are not given. In a few of the readings given the current was partly or wholly intermittent and such values are marked by a star. The smaller currents from point no. 4 were of this character and it is noticed that their value is less than what an agreement with the other results would require.

The above results, reduced to a pressure of 74 cm. and a temperature of 22° C., are represented by the curves shown in the lower part of Fig. 5.

The relation between the diameter of the points and the voltage

TABLE VII.

*Negative Discharge from Cylindrical Points with Hemispherical Ends.
Distance from Plate = 1.5 cm.*

Point Number.	1	2	3	4	5	6
Diameter in mm.	.0244	.039	.091	.174	.244	.50
Pressure in cm.	73.0	74.9	74.1	74.1	74.1	74.1
Temperature in °C.	19.0	21.5	26.5	27.0	27.0	27.0
Starting Potential.	1,125	1,475	1,975	2,775	3,100	4,650
Potentials in Volts, with Corresponding Currents in 10^{-7} Amperes.	1,250	2,000	2,000	3,000	3,500	5,000
	.3	4.1	.3	.6	7.2	10.6
	1,500	3,000	2,500	3,500	4,000	6,000
	1.8	16.5	5.0	1.5*	15.5	32.2*
	2,000	4,000	3,000	4,000	5,000	7,000
	5.4	39.1	12.5	13.9*	43.0	77.7
	3,000	5,000	4,000	5,000	6,000	7,500
	20.2	69.3	33.9	52.2	81.6	99.9*
	4,000	6,000	5,000	6,000	6,500	
	44.8	112.8	63.8	95.9	113.2	
	5,000	6,500	6,000	6,250		
	77.3	135.9	104.3	105.5		
	6,000		6,500			
	122.6		119.9			
	6,350					
	138.9					

required to produce a given current is again shown by the curves in the upper part of the figure. It is to be noticed that the voltage required to produce a given current here increases more rapidly with the diameter of the points than it did in the case of the positive discharge.

The results obtained throughout with the negative discharge do not permit of having the relation between the current, voltage and the diameter of the points, consistently represented by a formula as simple as served for the positive discharge. The discharge tending more to intermittence and irregularity seems to depend more on the surface conditions of the point than in the case of the positive discharge, and it may be too that some of the irregularity is due to the composite character of the gas, the current changing somewhat, especially at its lowest values, between the various components.

The relation between the diameter of the points d and the minimum potential M is represented by the formula $M=6,400\sqrt{d}+90$. Some values of M obtained from this formula are marked as triangles on the curve for $C = 0$ in Fig. 5.

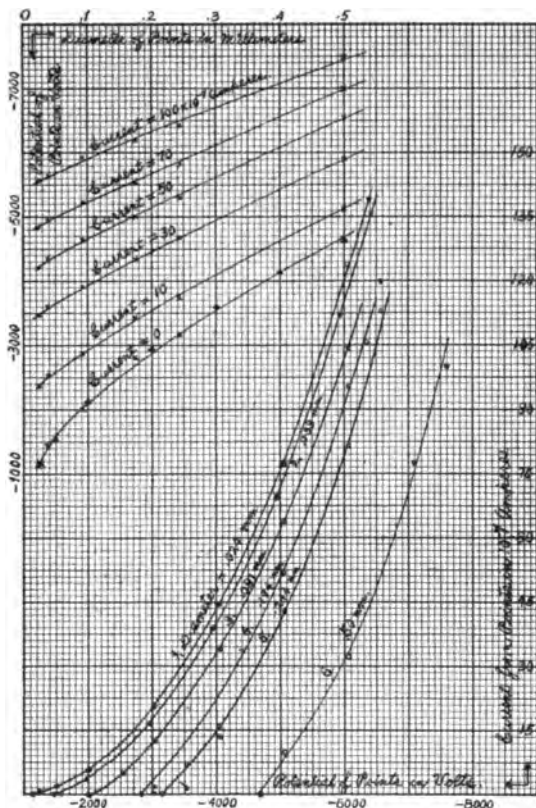


Fig. 5. Negative discharge in dry air from cylindrical points with hemispherical ends. Distance from plate = 1.5 cm. Pressure = 74 cm. Temperature = 22° C.

18. It was still more difficult to get a steady negative discharge while using the same points as above at a distance of 1 cm. from the plate. The few steady results that were obtained are given in Table VIII., and the corresponding values reduced to a pressure of 74 cm. and a temperature of 22° C. are shown graphically in Fig. 6. They appear rather irregular, possibly because of one of the last two points. The relation between the minimum potential and

the diameter of the points, as roughly given by the curve for $C = 0$ in the upper part of the figure, is represented by the formula $M = 5,300\sqrt{d} + 385$. The triangles on the curve named represent values obtained by the use of this formula.

TABLE VIII.

Negative Discharge from Cylindrical Points with Hemispherical Ends. Distance from Plate = 1 cm.

Point Number.	1	2	3	4
Diameter in mm.	.039	.091	.174	.267
Pressure in cm.	74.9	72.5	72.5	74.4
Temperature in ° C.	20.5	24.2	24.2	21.5
Starting Potential.	1,465	1,850	2,750	3,025
Potentials in Volts, with Corresponding Currents in 10^{-7} Amperes.	2,000	2 000	3,000	4,000
	7.7	1.1	3.0	35.2
	3,000	2,500	3,500	5,000
	30.3	9.9	23.1	89.7
	4,000	3,000	4,000	5,500
	71.5	23.7	46.2	133.1
	5,000	4,000	5,000	6,000
	130.9	64.9	104.5	171.6
	5,500	5,000	5,500	
	170.5	126.5	150.7	

19. The results obtained for the negative discharge from cylindrical points with hemispherical ends at a distance of 1.5 cm. from the plate, are given in Table IX. They are represented graphically by the curves in the lower part of Fig. 7, and the relation between the diameter of the points and the potential required to produce a given current, is shown by the curves in the upper part of the figure. The results for the two fine platinum wires, nos. 1 and 2 of Table VII., are included here also because of the agreement of the two sets of results for the smaller points, the curves being extended through them as broken lines.

The relation between the minimum potential M , and the diameter of the points d , is given in this case by the formula, $M = 5,545\sqrt{d} + 335$. The points shown by triangles on the curve for $C = 0$ in Fig. 7 represent values calculated by the use of this formula.

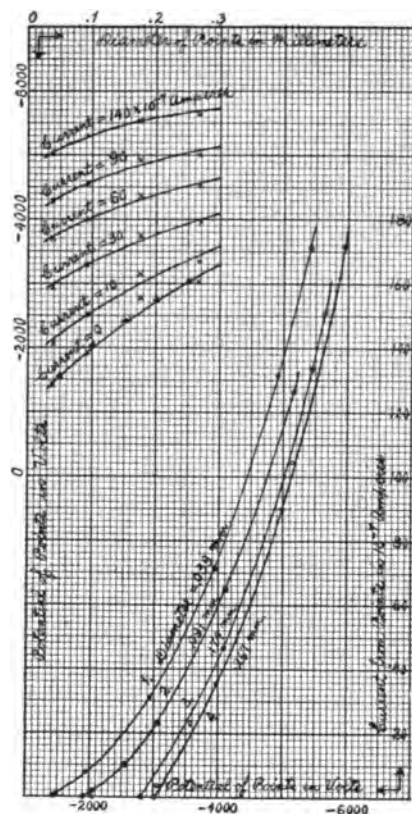


Fig. 6. Negative discharge in dry air from cylindrical points with hemispherical ends. Distance from plate = 1 cm. Pressure = 74 cm. Temperature = 22° C.

VARIATION OF DISCHARGE WITH PRESSURE.

20. Since the discharge is dependent upon the pressure of the air which varied from day to day, it was necessary to determine the magnitude of this effect so as to be able to reduce the results to a common pressure.

For doing this the apparatus was sealed so as to permit of its being partially exhausted. Sets of readings for both the positive and negative discharge were taken with a point .18 mm. in diameter at a distance of 1.5 cm. from the plate, with the air pressures at 51.8 cm., 63.4 cm., and 73.6 cm., the temperature being 19° C. The results obtained for the positive discharge are shown by the curves in Fig. 8.

TABLE IX.

Negative Discharge from Cylindrical Points with Plane Ends. Distance from Plate = 1.5 cm.

Point Number.	1	2	3	4	5	6
Diameter in mm.	.088	.19	.267	.51	.808	1.17
Pressure in cm.	73.7	73.7	73.7	74.8	73.9	73.9
Temperature in °C.	26.5	26.5	26.5	27.5	23.0	23.0
Starting potential.	1,850	2,750	3,100	4,350	5,300	6,350
Potentials in Volts, with Cor- responding Currents in 10 ⁻⁷ Amperes.	2,000	3,000	3,500	4,500	5,500	6,500
	.7	4.2	8.3	5.5	7.7*	7.7
	3,000	4,000	4,000	5,000	6,000	7,000
	14.1	23.7	17.9	18.2	22.6	30.8*
	4,000	5,000	5,000	6,000	7,000	8,000
	36.9	51.7	44.0	55.0	62.7*	77.0*
	5,000	6,000	6,000	7,000	8,000	8,500
	67.6	92.4	83.1	101.2	110.0	102.8
	5,500	6,625	7,000	7,350		
	90.2	122.1	127.6	121.0		

The relation between the pressure and the potential required to maintain a given current is shown for a number of currents, by the curves in the upper part of the figure. It is seen that for this range the potential increases linearly with the pressure. The variation of voltage with pressure is expressed for each current under its curve, as a fraction of the voltage required to produce that current at a pressure of 74 cm. This fraction only increases from .0087 for a current of zero to .0100 for a current of 100×10^{-7} amperes, and the increase was assumed to be a linear one. By means of this relation the voltage for each current obtained in all of the experiments was readily reduced to that necessary to produce the same current at a pressure of 74 cm., the fraction given above being the part of itself that any voltage has to be diminished for each centimeter that the pressure was above 74 cm.

The results obtained for the negative discharge at the different pressures are shown in Fig. 9. From the curves in the upper part of the figure it is seen that the variation of the voltage with the pressure changes for the different currents from .0096 to .013 part of the voltage required to produce the given currents at 74 cm.

pressure. The increase in this fraction was assumed to be a linear one and the correction for pressure was applied to each of the results for the negative discharge in the same way as is explained above for the positive discharge.

VARIATION OF DISCHARGE WITH TEMPERATURE.

21. To get the magnitude of the corrections that must be applied to reduce the results to a common temperature, potential current

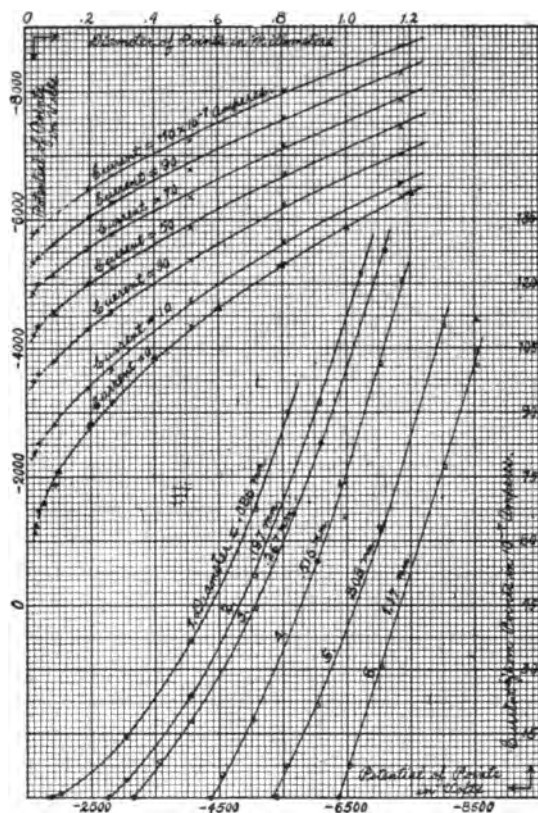


Fig. 7. Negative discharge in dry air from cylindrical points with plane ends. Distance from plate = 1.5 cm. Pressure = 74 cm. Temperature = 22° C.

curves were obtained for both the positive and the negative discharges with the apparatus at two different temperatures, using a point .091 mm. in diameter at a distance of 1.5 cm. from the plate.

The temperatures used were about 23°C . and about 0°C ., the first being the ordinary temperature of the room, and the second being obtained by opening the laboratory windows and letting the whole

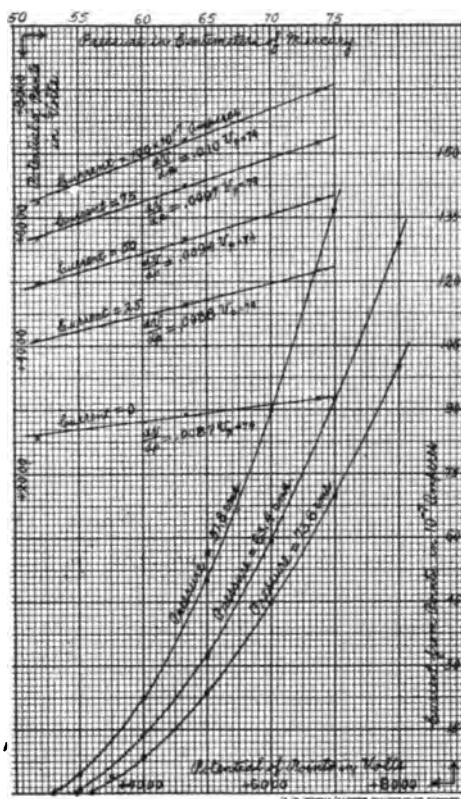


Fig. 8. Positive discharge in dry air at different pressures. Cylindrical point with spherical end. Diameter = .18 mm. Distance from plate = 1.5 cm. Temperature = 19°C .

room cool to that temperature. Three sets of readings were taken and the results of one of these are shown by the curves in Fig. 10. It is seen that at a lower temperature a larger voltage is required to produce the same current. A peculiarity appears in this set of readings for the positive discharge, since the curves for the two temperatures approach coincidence at the starting point. This did not repeat itself in the other two sets of readings taken, and the average effect calculated from all of the results was thought sufficiently accu-

rate for the purpose in hand. It was thus found that for every 1° C. decrease in the temperature, the voltage required to maintain any current increases by approximately .0018 part of itself for the positive discharge and by .0028 part of itself for the negative discharge. The effect may be due for the most part to a change in the air density, but the values are not sufficiently accurate to decide this. The number obtained for the negative discharge is in agreement with this supposition.

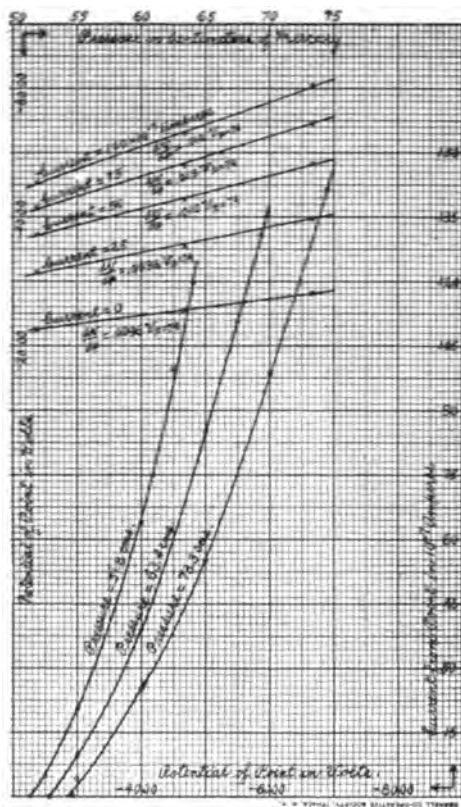


Fig. 9. Negative discharge in dry air at different pressures. Cylindrical point with spherical end. Diameter = .18 mm. Distance from plate = 1.5 cm. Temperature = 19° C.

The temperature and pressure corrections found in each case by the use of a point of one size only were assumed to hold alike for points of all sizes. The observations were, however, reduced to a pressure

and a temperature near to the mean of the conditions prevailing, so that the total correction applied was quite small in most cases and in only a very few was as high as two per cent.

GENERAL REMARKS.

22. The ends of the wires used in the experiments were by no means free from minor irregularities in shape, but from the regularity of the results obtained with them it would appear that the

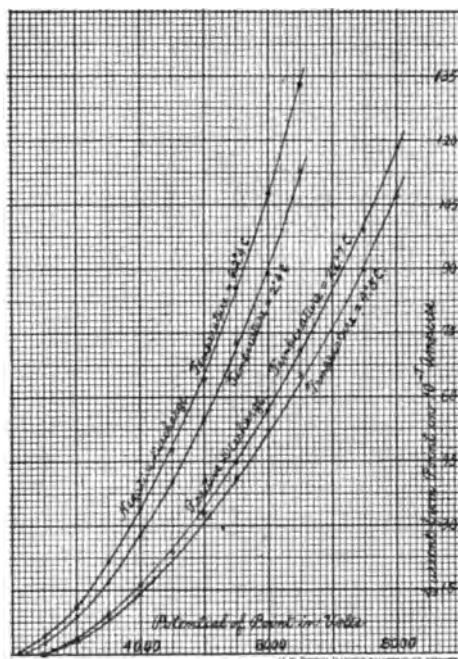


Fig. 10. Effect of temperature upon the discharge from a cylindrical point with a rounded end. Diameter = .091 mm. Distance from plate = 1.5 cm. Pressure = 74.85 cm.

discharge is fairly independent of such irregularities as are small compared to the size of the point, and depends only upon the general size and form of the point. Indeed the results obtained with the smallest points indicate that with them the ends may have large irregularities without affecting the results greatly.

The number that must be subtracted from the minimum potentials to make the results, up to a certain limit, proportional to the square

roots of the diameters of the points, were found for the best agreement in the three cases of the positive discharge, to be 755, 675 and 705. If the formulæ hold for minute values of the diameters, the above numbers indicate the voltage necessary to start a discharge for $d = 0$. The corresponding numbers obtained for the negative discharge, though far from being alike, average less than a half of the above numbers for the positive discharge. The ratio of the potentials necessary to start the two discharges with infinitesimal points would thus appear to be even larger than with points of a finite size, and this is in agreement with what is noticed, *i. e.*, that as the points get larger the two kinds of discharge start at more nearly the same potential relatively.

SUMMARY.

23. It has been shown how it is possible to select conditions for the discharge from pointed conductors so that the numerical results obtained may readily be reproduced with new points and apparatus. This is made possible for the most part by using points of such a simple and definite shape that they may easily be duplicated with sufficient accuracy. For this purpose it has been found that points made of cylindrical wires of a sufficient length, with their ends either rounded or plane are very convenient and give regular results depending only upon the diameters of the wires.

Curves are given from which it is possible to find the current that will flow in dry air, under the normal conditions given from a point of any size up to 2 mm. in diameter, for any given potential. Corrections are given also by means of which it is possible to extend the results to any temperature usually found in the room and to a considerable range of pressures near that of the atmosphere.

Voltages may be determined with fair accuracy by measuring the current flowing from a point of known size and using a potential current curve drawn for the particular point by the aid of the results here given.

The potential required to start a discharge and the diameter of the point are related, at least for a limited range, so that the minimum potentials minus a constant are proportional to the square roots of the diameters of the points. This relation holds especially well for points with plane ends.

The relation between the current from a point and its potential may be represented quite well for the positive discharge from any point by Warburg's formula, $C = aV(V - M)$. This formula is extended to include at once points of all sizes, by changing the constant " a " to $a(1 + bd)$, where d is the diameter of the point and a and b are new constants.

By embodying the relation between the minimum potential and the size of the point into this formula, it becomes possible by its means to calculate the current which will flow in dry air from a cylindrical point of any diameter when this is at any given potential and placed at a definite distance from a plate.

In a paper to follow the results will be given which have been obtained for the discharge from conical points of a definite angle and from steel needle points, as well as some other results on the discharge from points.

THE PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
June 1, 1907.

POTENTIOMETER INSTALLATION.

ESPECIALLY FOR HIGH TEMPERATURE AND THERMOELECTRIC WORK.

BY WALTER P. WHITE.

THE increasing interest shown in high temperature research by scientific workers in different fields has suggested the publication of various methods which have recommended themselves in this laboratory.¹ The present paper deals with the thermoelectric measurement of high temperatures, and more particularly with the apparatus auxiliary to the thermoelement, which consists for the most part of commercial potentiometers of familiar type, with the usual accessories. In the installation of this apparatus, several simple modifications have greatly increased the efficiency, not only for the more specialized work of the laboratory, but for general work as well. The present paper, therefore, may prove of interest to some not especially concerned with high temperature research.

The work for which this apparatus is specially arranged is the determination of melting points and similar thermal phenomena in silicates and other refractory substances. The determinations are carried out by the familiar method of Frankenheim. A charge of the substance under investigation is heated in an electric furnace, whose temperature is continually measured and controlled; the variations in the temperature difference between charge and furnace indicate the changes going on in the charge. This method will soon form the subject of another article, and need not be further

¹ Brief descriptions of some of the apparatus and methods have already been given in connection with the published work of the laboratory as follows: Of the furnace and thermoelements, Day and Allen, Carnegie Institution Publication No. 31, *PHYS. REV.*, 19, 17, 1904; of the general methods of measurement, Carnegie Institution Publication No. 31 (partly reprinted in *Zeit. f. Phys. Chem.*, 54, 1, 1905); also Allen, White and Wright, *Amer. Journ. Sci.*, 21, 89, 1906; Day and Shepherd, *Amer. Journ. Sci.*, 22, 265, 1906; Allen, Wright and Clement, *Amer. Journ. Sci.*, 22, 385, 1906; of the treatment of thermoelements, W. P. White, *PHYS. REV.*, 23, 449, 1906 (*Phys. Zeitschr.*, 8, 325, 1907).

considered here. The problem which it sets in electrical measurement may be stated as follows :

(a) Temperatures up to 1600° must be read to $.1^{\circ}$; with a platinum-platin-rhodium thermoelement, $.1^{\circ}$ corresponds to about one millionth of a volt.

(b) The materials of the furnaces, and also the air, become ionized and conduct electricity at the temperatures generally employed. The potential difference in the heating coils is about 100 volts, that is, one hundred million times the allowable error of the measurements, yet leakage from the coils must not be allowed to affect the measuring system.

(c) The measurements consist in following two or more continually changing temperatures. The only effective way to accomplish this is to read the various temperatures in rotation at definite intervals. Two or more readings per minute are usually needed. The experimenter must also have time to note carefully the progress of his experiment, to regulate the temperature of the furnace, and so forth, and must still be freed as far as possible from hurry or fatigue, since mistakes can seldom be corrected during the progress of the heating. Manipulation must therefore be simplified and the apparatus must respond as quickly as possible. Quickness and simplicity, then, without sacrifice of sensitiveness or accuracy under trying conditions, are the qualities required of the electric measuring apparatus in silicate work. Even if less imperatively needed, they are obviously desirable in other work as well.

Melting point determinations at high temperatures have hitherto been mainly made either with the platinum resistance thermometer or with the direct reading thermoelectric pyrometer. Neither of these instruments meets the demands of silicate work.

The direct reading pyrometer lacks sensitiveness, since intervals smaller than 5° cannot be read with certainty.¹ The resistance thermometer is well known to be poorly adapted for temperatures

¹ This is the unavoidable error of a carefully calibrated instrument in first-class condition. Ordinarily, very much larger errors are present. For instance, the scales in different instruments from the same maker sometimes differ 6° at 1000, and thermoelements of the best make may vary 12° . Calibration errors of 10° at 1000 have also been observed in new instruments, while a surprising amount of care is needed to avoid much greater errors from faulty contacts.

above 1000° , and is therefore out of the question for nearly all silicates. (The stretching of the wires when hot, failure of the insulation and the disintegration of the platinum at higher temperatures, all affect the readings of the resistance pyrometer much more than those of the thermoelement.) Another disadvantage of the resistance thermometer in melting point work at all temperatures seems less generally appreciated. This is the relative bulk of the working portion, which must be completely covered by the substance examined, and which therefore necessitates using large quantities of material. Some of our best melting point determinations at high temperatures are now obtained with about 1 cu. cm. of substance, in which the bare thermoelement is directly inserted. For work of this character, the resistance thermometer is obviously out of the question.

The thermoelement read with a potentiometer meets all requirements of the present work. Readings can be made with practically the same ease as on a direct reading instrument, so that whatever difficulty there is in this direction is chargeable to the nature of the measurements, not to the apparatus. When properly installed, the potentiometer will remain for months ready for instant use, with no other attention than an occasional oiling of the switches. The accuracy is, of course, that of the thermoelement, and has been sufficient for all work thus far undertaken. The elements are exposed to high temperatures for the shortest possible period and are used either in glazed porcelain tubes or in furnaces free from commercial platinum. Under such conditions, deterioration, though not entirely prevented, is slow.¹ By measuring to a millimeter the depth of insertion in the furnace, and by comparing occasionally with carefully kept standards, the relative error of the temperature measurements can be reduced to $\frac{1}{3}^{\circ}$, which is a little less than other errors inherent in the work.

Partial Direct Reading. — Simplicity of manipulation and quickness are promoted by making the maximum use of a direct reading instrument, the galvanometer. Since a galvanometer alone, in the form of a voltmeter, is sufficient for rough measurements with

¹ In twenty determinations near 1350° , occupying about 10 hours, an element inserted 17 cm. in the furnace fell a little over 1° .

thermoelements, a moderate increase in its efficiency is all that is needed for the most refined work. Yet when a potentiometer is added to secure greater efficiency, the whole burden is often thrown upon the potentiometer, and the galvanometer is used merely to indicate when a balance is obtained. This practice has some obvious advantages, but is not justified where rapidity is important. If the galvanometer is provided with a scale reading directly in micro-volts, and is used through a rather wide range, the potentiometer adjustments may be confined to the larger units and greatly reduced in number. The quickness and simplicity of exclusively direct reading are thus approached with no sacrifice of accuracy.

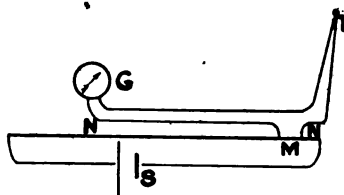


Fig. 1. To accompany formula 1.

A necessary requirement for this system is, of course, constant galvanometer sensibility, which is not found in ordinary potentiometer installations. I have elsewhere¹ shown how potentiometers can easily be constructed so as to give constant galvanometer sensibility. For ordinary instruments, and for the range needed in thermoelectric work, a sufficient approach to it can be obtained by inserting an extra variable resistance in the galvanometer circuit, as shown at R_A in Fig. 4. The operation of this resistance is as follows: Let Fig. 1 represent a simple potentiometer installation, where G indicates the resistance of the galvanometer, and T that of the thermoelement, whose electromotive force is balanced against the fall of potential along the resistance, M , in the main circuit. S is the storage cell of the main circuit, $M + N$ the total resistance in that circuit. The electromotive force of the thermoelement may be considered as equal to the sum of two others; one is equal and opposite to that given by the potentiometer setting, and has the effect of neutralizing the potentiometer electromotive force completely as far as any current through the galvanometer is concerned; the other, Δe , is the unbalanced electromotive force which is to be measured by the galvanometer, and which, by the well known principle that each electromotive force in a circuit produces its own

¹ Zeitschr. f. Instrumentenkunde, 27, 210, 1907.

current regardless of all others present, gives a current equal to

$$T + G + \frac{MN}{M + N} \quad (1)$$

Constant galvanometer sensibility is therefore secured by keeping the resistance $T + G + \frac{MN}{M + N}$ constant.

In measuring the comparatively small electromotive forces of platinum thermoelements, the resistance $\frac{MN}{M + N}$ differs but little from M ; hence sufficient compensation is obtained if resistance is subtracted from the ballast, R_A , equal to that added to M in setting the potentiometer. An ordinary switch rheostat of very moderate accuracy is sufficient. The labor of making the adjustments is usually slight. For instance, if the resistance of the galvanometer circuit is 500 ohms and an accuracy of 0.5 per cent. is desired in reading the galvanometer, the resistance must not vary more than 2.5 ohms. The auxiliary must therefore be changed whenever the potentiometer resistance, M , has altered 5 ohms. In a potentiometer of 20,000 ohms total resistance, 5 ohms correspond to 500 microvolts, or from 40 to 50° with a platinum-platinum-rhodium thermoelement, and the adjustment will not need attention oftener than once in 15 minutes in ordinary work. In a potentiometer of 2,000 ohms total resistance, on the other hand, 5 ohms will correspond to from 400 to 500°; the adjustment can be made before the observations begin, and will then need no further attention. A potentiometer resistance moderately — but only moderately — low compared to that of the rest of the circuit may therefore be of advantage where constant galvanometer sensibility is desired. (A rather high resistance of the whole circuit is also desirable to reduce the effect of accidental variations in resistance due to the changing temperature of the thermoelement, to defective contacts, etc.) In classes of work where widely differing electromotive forces are to be measured in succession, the difficulty of maintaining constant galvanometer sensibility obviously increases, and the need is greater for a potentiometer of low resistance, or, better still, of constant branch circuit resistance.¹

¹ H. B. Brooks has also, in his "deflection potentiometer" (Bull. Bureau of Standards, vol. 2, p. 225, 1906), made a systematic attempt to gain speed by increasing

The usefulness of the above method of relying largely upon the galvanometer will of course vary greatly under different circumstances. In melting point determinations, constant galvanometer sensibility is not only very easy to obtain, but is especially important, for the following reasons: (1) In the rapid reading of varying electromotive forces at definite time intervals, an exact balance of the potentiometer is out of the question. The galvanometer follows the varying electromotive force¹ and needs about as much time to reach its moving equilibrium as it requires to come to rest. Hence the nearest attainable approach to a balance is a potentiometer setting made a number of seconds before the time of reading. When that time arrives, the galvanometer nearly always shows a deflection which must be added to or subtracted from the potentiometer reading. Some use of the galvanometer as a deflection instrument is therefore unavoidable. The quantities read can, if desired, be kept within 20 microvolts, for which a sensibility constant to 5 per cent. is ample. (2) When once deflections of this magnitude have been provided for, however, an increase of the range to 100 or 200 microvolts causes very little further trouble. Moreover, in melting point determinations, such increase is especially advantageous. This is due to the fact that the temperature intervals concerned—those between the different elements as well as between successive readings of the same element—are usually more than ten and seldom over 200 microvolts. With the narrower galvanometer range, a separate setting of the potentiometer must be made twice each minute, involving a preliminary estimate, the setting of two or three switches, and afterward the addition of the readings obtained from both instruments. With the more carefully adjusted galvanometer, the potentiometer requires only to be advanced one unit every few minutes and the deflections are read and recorded directly from the scale. The saving in numerical work of various kinds is even more important than in switch manipulation, though

the use of the galvanometer. The small sensitiveness of this apparatus, and some of the other difficulties which Mr. Brooks ingeniously avoids, are due to the use of an insensitive pivot galvanometer, and, as his own discussion implies (p. 238) are not inherent in the method.

¹ Lagging behind it by a time interval which is approximately equal to T/π , if the galvanometer, of period T , is critically damped.

this latter may often be diminished ten times. For the more difficult kinds of work, where readings are numerous, or an especially careful regulation of the furnace is desired, this saving is indispensable.

The price paid for the advantage is merely a little attention to the galvanometer sensibility, which may change slightly with temperature, and becomes irregular if faulty contacts are permitted in the circuit. A verification of the sensibility, however, can be made at any time and requires nothing further than to change the potentiometer setting and note the resulting change in deflection.

The galvanometer sensibility should obviously have an integral as well as a constant value. This can readily be secured by varying the scale distance, which is also a convenient way to correct slight

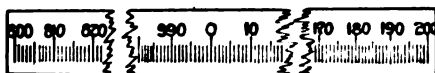


Fig. 2.

Fig. 2. Arrangement of the scale. The numbering is direct, everywhere increasing with increasing E.M.F., yet the reading is zero at the middle of the scale, and readings less than zero are clearly indicated. The figures to the left are, following a common practice, in red, which often shows the direction of a deflection too rapid to permit of reading the numbers.

Fig. 3. To accompany formula 2.

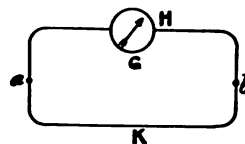


Fig. 3.

variations in the sensibility. Fig. 2 shows the arrangement of the scale. The method of numbering has some obvious advantages.

Protection against Leakage. — The avoidance of leakage errors is made especially difficult in silicate work by the combination in the furnace of high voltage and poor insulation — the latter due to unavoidable electrolytic conduction at high temperatures.

In order to have leakage affect the galvanometer reading, there must be a failure of insulation in at least two points of the circuit. The law governing the magnitude of the effect may be found as follows:

In Fig. 3, let a and b be the (very high) resistances through which the leakage takes place; let V be the external voltage causing the leak. Let G be the resistance of the galvanometer, and H the remaining resistance which lies with the galvanometer in the circuit

between a and b . Let K be the resistance of the other path from a to b . The total leakage current, L , will equal $V/(a + b)$ and will not be appreciably affected by the relatively small resistances in the circuit. The error caused by L will, however, depend on these resistances. The portion of the current passing through the galvanometer is

$$L \frac{K}{H + K + G}.$$

The resulting error, in microvolts, will be equal to this current divided by the current which is produced by one microvolt, that is :

$$\frac{LK}{H + K + G} \div \frac{1}{H + K + G} = LK = \frac{VK}{a + b} \quad (2)$$

Leakage errors may therefore be diminished in three ways : *first*, by increasing either a or b , that is, by improving the insulation ; *second*, by diminishing the resistance of the alternative path, K ;¹ *third*, by diminishing V . This last is the most effective way of removing leakage errors. It can be accomplished by an equipotential shield, a device whose essential features are shown in Fig. 4. The potentiometer, galvanometer, and all other apparatus belonging to the measuring system, are set on metal plates ; the leads are completely supported by wires ; the plates and the wires are connected so as to form a continuous conductor which is extended into the furnace, where it includes the crucible and also passes between the thermoelement and the furnace cover. This conductor thus interposes between the measuring system and every external electromotive force, while it needs itself but slight insulation in order to be an equipotential surface ; the most troublesome leakage, that from the high voltages in the furnaces and elsewhere, is therefore absolutely prevented.²

¹ This can often be accomplished by a mere transposition of apparatus, and does not necessarily demand a reduction of the total resistance. The leakage error may obviously be considerably influenced by the mere order in which the different pieces of apparatus stand in the circuit. Formula 2 explains why leakage is sometimes less with potentiometers of low resistance and also shows that this result may be accidental, according to whether the potentiometer resistance is included in the portion K of the circuit. It is always possible, by the method of page 343, to insert resistance so as not to increase the leakage error.

² The equipotential shield was suggested by C. T. R. Wilson's electroscope (Proc. Roy. Soc., 68, 152, 1901). H. P. Brooks has also applied the same principle in a different way to potentiometer work. (Loc. cit.)

The presence of external leakage may be tested by watching the throw of the galvanometer when *both* terminals of the heating circuit are suddenly disconnected. This test is applied from time to time in order to avoid the possibility of error due to accidental contact with or breaks in some part of the shield. If the shield is in

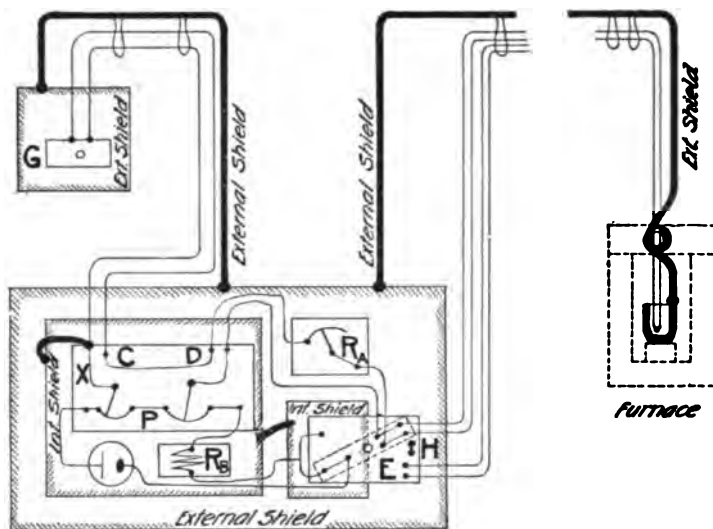


Fig. 4. Very diagrammatic representation, partly in plan, but with the furnace in vertical section, of the measuring apparatus, showing the relations and connections of the two leakage shields. The cold junctions and standard cell are omitted. *G*, galvanometer, *R_A*, auxiliary resistance (for adjusting sensibility); *R_B*, ballast-resistance; *P*, potentiometer; *E*, exchanging switch; *H*, short-circuiting link, for zero adjustment.

perfect condition, of course no external leakage error can possibly occur. As a rule, this test gives zero results during the winter, even in the absence of a shield. This is due to the fact that insulation then fails at but one point in the circuit, and of course does not indicate perfect insulation in the furnace itself.

The use of a complete shield is often inconvenient or impossible. In such cases, a partial shield can be employed, which is connected directly to the potentiometer circuit. Such an arrangement does not prevent the leakage, but guides it to some desired point, thereby reducing the resistance, *K*, of equation (2). Its effectiveness is more dependent upon good insulation than is that of the complete shield.

Partial shields have been used in three cases: (1) It is sometimes inconvenient to extend the shield into the furnace. By connecting the shield to the thermoelement as near the furnace as possible, K is diminished to the resistance of a few centimeters of the thermoelement wire, and satisfactory results are often obtained. The other cases arise where complete shielding is prevented because the source of leakage is in metallic connection with the circuit. One of these occurs where the voltage or current of a high potential circuit is being measured. The shield is then connected to the junction of the potentiometer circuit and the circuit in question. K is now zero, and the external protection is complete. Another case arises in the protection of the potentiometer system from leakage out of its own storage cell, which we have found by no means negligible in the humid summer months. The arrangement used is as follows:¹ The shield, lying under storage cell, potentiometer and ballast resistance, is connected, as shown in Fig. 4, to the *lower* terminal of the branch circuit, that is, the one nearest an end of the potentiometer wire. This terminal should be

¹ Those especially interested will readily find in the following equations an explanation for the arrangements here described. These equations are obtained by considering that an electromotive force in the leakage path equal and opposite to the normal electromotive force in the circuit between the two ends of that path would reduce the leakage to zero, and therefore, that the current produced by such an electromotive force is equal (but opposite) to the leakage current. The effect of such a current upon the galvanometer is easily calculated. If V is the storage cell voltage (in microvolts), L the leakage resistance, M the fractional portion of the circuit across which leakage occurs, T the resistance of the thermoelement, C the resistance between terminals of the branch (galvanometer) circuit, then the error in microvolts is, for leakage between two points, both in the main circuit, not including C ,

$$\frac{VM}{L} MC \quad (3)$$

or two such points, including C between them,

$$\frac{VM}{L} (1 - M) C \quad (4)$$

for leakage from the main circuit to a point between thermoelement and galvanometer, roughly,

$$\frac{VM}{L} T. \quad (5)$$

The efficiency of the above arrangement is dependent upon the small value of the voltage measured. A different disposition would probably be preferable where electromotive forces of the order of 1 volt are to be measured.

made as low as possible, that is, no ballast resistance should intervene between it and the battery. (Ballast resistances are found at this point in some potentiometers. They are, however, objectionable¹ for other reasons, and can easily be short circuited or removed.) The result of this arrangement is that leakage from the battery cannot reach any portion of the circuit outside the apparatus resting on the shield, while within the shield, such leakage as may occur will, in general, produce the minimum amount of error.²

Minor Details.—In all refined galvanometer work, provision must be made for eliminating the accidental electromotive forces of the circuit. In thermoelectric work, this requires that the large electromotive forces, those of the thermoelement and battery, be momentarily removed and the circuit then closed. This operation is accomplished by a switch of simple construction, which shifts the terminals of the potentiometer and galvanometer circuit from the thermoelement to a short-circuiting link, and at the same time opens the battery circuit at one point.³ A further motion of the handle makes connection with a second and a third thermoelement. Provision for the two essential operations, zero adjustment and exchange of thermoelements, is thus made by one simple piece of apparatus. The correction for the accidental electromotive forces is applied by simply adjusting the scale to read zero, and the trouble of making a numerical correction is thus avoided. A slow motion for this

¹ Principally because their presence may restrict the choice of a storage cell to one possessing exceptionally high voltage.

² Leakage into the balance resistance is further prevented by suspending this from its own metallic terminals. Such leakage, and also leakage along the potentiometer top from point to point in the circuit, will diminish with the resistance of the potentiometer, and may thus be made negligible. We have no evidence, however, that such leakage in a potentiometer of 10,000 ohms to the volt need be serious. Leakage to the direct junction upon the potentiometer top of thermoelement and galvanometer leads (*CD* in Fig. 4) will be serious only if the resistance of the thermoelement is high (with a constantan element, for instance), and can then be prevented by removing that junction from the potentiometer top altogether.

³ If this point is near the lower end of the potentiometer—that is, near *x* in Fig. 4—leakage at the switch will be prevented while the battery circuit is closed. Trouble from leakage may arise, however, during the zero adjustment, but this can be detected by occasionally disconnecting the other battery terminal. If the regular opening of the battery circuit is at the high end and the two leads are separated from each other and from the rest of the switch by an extension of the internal shield, as indicated in Fig. 4, there will be no danger from leakage at the switch whether the circuit is open or closed.

purpose, sufficiently delicate and entirely free from lost motion, has been found very easy to make. The scale is drawn along against the tension of a coiled spring by winding a cord upon a bent brass rod. Our regular telescopes have a slow motion supplied by the maker.

In this method of compensation it is not the accidental electromotive forces, but the deflection due to them, which is directly compensated, and the adjustment, therefore, is incorrect, if the removal of the thermoelement appreciably changes the resistance of the circuit. This difficulty is inappreciable with platinum thermoelements; with those of constantan, other methods are used.¹

None of these methods compensates the electromotive forces in the thermoelement leads, and in some portions of the switch itself. All such forces are therefore diminished by making these portions of the circuit entirely of copper. The only exception is the springs and bearing surfaces of the switch, which, for mechanical reasons, are made of manganin, a material at once hard and of small thermoelectric power compared with copper.

The important contacts on the potentiometer are kept in good condition by oiling every few weeks with typewriter oil, in accordance with a suggestion from the Reichsanstalt. A reasonable amount of attention to other contacts in the circuit is also necessary in order to maintain constant galvanometer sensibility.

The cold junctions, protected by glass tubes, are in a bath which is usually maintained at 0° by means of ice. To insure the junctions being at the temperature of the ice, fine copper leading-in wires are used, while oil or paraffin inside the tubes and water outside improve the thermal contact between the ice and the junctions.

¹ A. D. Palmer (PHYS. REV., 21, 72, 1905) compensates the electromotive forces directly by an auxiliary potentiometer. This method, in the one case where its complication is needed, that is, where the resistance of thermoelement is high, evidently fails unless the galvanometer is at zero on open circuit. Practically, therefore, in employing it, two separate adjustments must be made, of which that on open circuit, with the galvanometer undamped, is somewhat tedious and altogether inadmissible in rapid work. In our laboratory, therefore, another method is employed, and the circuit is closed for zero adjustment through a resistance equal to that of the thermoelement which is then removed from the circuit. The value of this resistance evidently need be only approximate, but it must be so wound as to be free from thermoelectric force — a condition easily realized.

The constancy of the storage cells is increased by shielding them from temperature changes with a wrapping of cotton wool.

Insulation of the standard cells is promoted by suspending them from their own leads.

Since the zero adjustments, as well as the readings, are made on a closed circuit whose resistance is kept constant, the galvanometer is adjusted so as to be damped entirely by the reaction of the circuit, and maximum sensibility is thus obtained. To insure proper damping while the circuit resistance is increased during the comparison of storage and standard cell, a coil is connected between appropriate terminals of the standard cell and galvanometer. This coil has no effect except when the cell is connected to the potentiometer. It then acts as a shunt to the galvanometer, giving critical damping together with a decrease (here unobjectionable) in sensibility.

The galvanometers are placed upon Julius suspensions, which are enclosed against air currents. We have found that the position of the center of gravity with reference to the galvanometer head does not appreciably influence the steadiness, that is, the oscillations which the supports perform about their centers of gravity are not of a character to affect our moving coil galvanometers.

Galvanometer Requirements. — A satisfactory adjustment of the potentiometer system, according to the methods above described, requires a galvanometer which, while not necessarily of extraordinary quality, is well adapted to its work. Leading instrument makers, in this country at any rate, will, as far as possible, furnish instruments to meet specified requirements.¹ The necessary or desirable galvanometer constants are as follows:

(a) *Sensibility.* — The most convenient method of defining the sensibility of a galvanometer is to give the deflection in millimeters produced by unit current or voltage with the scale distant 1 meter from the mirror. For sensitive instruments, the unit voltage is 1 microvolt. An instrument, then, which gives a millimeter per microvolt at 1 meter's distance has a sensibility equal to 1.

With reasonably good optical arrangements and fair steadiness, a sensibility of .3 is quite sufficient for silicate work. Half a scale

¹For a more detailed discussion of the problems of galvanometer adjustment, see "Every Day Problems of the Moving Coil Galvanometer," *PHYS. REV.*, 23, 382, 1906.

division will then correspond to a microvolt, and the scale distance will usually be more than 1 meter. A sensibility of .5, with 1 scale division per microvolt, is a little more desirable, and may be necessary for reading to tenths of microvolts, or with poor optical arrangements.

(b) *Period.* — A period of 10'' is sufficient only for the simpler portions of our work, and scarcely satisfactory in those. 5'' is short enough for almost anything, though a still shorter period is often convenient.

(c) *Resistance.* — The necessary total resistance of the galvanometer circuit depends largely upon the type of potentiometer. The resistance of platinum thermoelements at different temperatures varies an ohm or more. Hence for sensibility constant to .5 per cent. a total branch circuit resistance of 200 ohms is desirable. For a potentiometer of high resistance whose branch circuit is (as usual) not constant, the total resistance should be 500 ohms or more (see page 338). This requirement is less important if the range of interpolation is small (see page 339).

Satisfactory values, then, are, a sensibility of .3, a period as short as 5'', and a total or critical resistance of 200 ohms, which should be increased to 500 ohms or more with an ordinary high resistance potentiometer. Greater sensibility, greater quickness and higher resistance are more or less in the nature of luxuries. As far as the galvanometer is concerned, these three constants are antagonistic. For a given type of instrument, an increase in one involves a sacrifice of the others. A high resistance potentiometer (10,000 ohms to the volt) may in thermoelectric pyrometry contribute as much as 170 ohms to the galvanometer circuit; with 500 ohms total resistance, then, over 300 may be in the galvanometer alone, a condition which greatly facilitates the attainment of short periods in galvanometers with weak magnets.¹

We have found no great difficulty in securing the above performance with several different types of galvanometer, although the majority of the instruments now on the market do not seem to permit of anything very much better. With a low resistance potentiometer the reduction of the total resistance to 200 ohms easily

¹ Every Day Problems, etc., pp. 384, 387.

allows, with the same type of instrument, a sensibility of .5 or a period as short as four seconds. A much better galvanometer performance is certainly possible,¹ although it seems worth while to emphasize the fact that such increase, while desirable, is not necessary for most thermoelectric work and would be dearly bought at the cost of even a slight sacrifice of constancy or steadiness, such as is apt to result from too great delicacy of construction. A considerably better performance, however, than the one above described should be attainable along with ample steadiness and constancy.

Either an especially good galvanometer or a low resistance potentiometer, therefore, allows a short period and excellent sensibility. With an ordinary galvanometer and a high resistance potentiometer a satisfactory arrangement can still be obtained, though it requires fair steadiness and good optical arrangements.

The Potentiometers. — Three reasons have been given for desiring potentiometers of low resistance: The internal leakage is less; better results can be obtained with an inferior galvanometer; and especially, the adjustment for constant sensibility is more easily made. This latter advantage is, of course, far more completely secured in a potentiometer with automatically constant branch circuit resistance. In point of fact, a switch potentiometer constructed to have either low resistance or a constant branch circuit may just as well have the other also.²

Of far greater importance, however, are ability to set the potentiometer quickly, and freedom from uncertain contacts, which may affect the resistance of the galvanometer branch. In both these respects the slide wire potentiometer is deficient, so much so as to be very unsatisfactory for melting point work. That it takes more time and attention to set a pointer exactly on a mark than to put a switch somewhere upon its appropriate button is perhaps a minor disadvantage, but the time required to wind the drum of a slide wire instrument from one position to another absolutely precludes simultaneous work with two elements differing much in temperature, while the resistance of the sliding contact is, in ordinary instruments, so uncertain as to make constant sensibility impossible. Devices designed to over-

¹ Every Day Problems, p. 388.

² Instrumentenkunde, loc. cit.

come this difficulty are at best open to the objection of introducing an additional complication. It may not be superfluous to call attention to the fact that apparatus which under most circumstances would be quite satisfactory, may fail in melting point work, where the demand for certainty of operation is so much greater. A single faulty observation may destroy the value of a thermal curve several hours long, and the frequent readings leave no time to correct even slight or temporary defects in the apparatus.¹

Hitherto, all-switch instruments have necessarily been made with high resistance on account of the internal contacts at some of the switches. Since the disadvantages of high resistance are small compared to those presented by the slide-wire, the older instruments in this laboratory are Wolff potentiometers of 10,000 ohms to the volt.

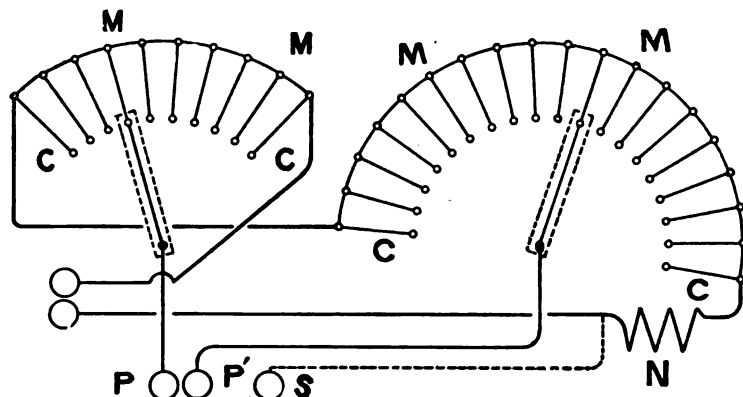


Fig. 5. Simple low resistance potentiometer, of sufficient range, and very convenient for high temperature thermoelectric work. The branch circuit is kept of constant resistance by the coils, CCC, and the galvanometer sensibility is therefore constant. MMN, main circuit potentiometer coils. PS, standard cell connection. A key and a switch are here omitted for simplicity.

There should now be no difficulty in getting all-switch potentiometers possessing not only the low resistance of the slide wire instrument, but a constant branch circuit as well.² The slide wire

¹ Much of the difficulty in regard to galvanometer sensibility and contact resistance disappears if the familiar method is adopted of noting the varying times at which regular and integral values of the electromotive forces are reached; but this method is considerably more laborious where one thermoelement is being read, and often inadmissible with two or more.

² Instrumentenkunde, loc. cit.

instruments might still have an advantage in the matter of cost, but in this respect also they can be excelled, provided the range of the switch potentiometer is limited to the requirements of thermoelement work. Such an instrument was designed and ordered for this laboratory in April, 1906, and is now in use (Fig. 5). It has only two main switches and measures from 100 to 18,900 microvolts. The coils, *cc*, are so adjusted as to keep the resistance between *P* and *P'* always constant. Since the simplest kind of switch will suffice for an instrument of this character, the total cost should hardly exceed that of the coils. Another decade would be desirable,¹ but the advantages of the instrument here figured are believed to be, for melting point work, on the whole superior to those of the usual types. One of these is the possibility of using the instrument as a double potentiometer,² a great advantage in work requiring the simultaneous measurement of very different temperatures.³

The general usefulness of the resistance thermometer is increased by the fact that ready-made outfits varying in accuracy and elaborateness can be bought for different purposes. For the thermoelement there is at present in commercial instruments practically nothing between the crude, direct-reading voltmeter and the expensive and yet relatively inconvenient five-decade potentiometer with a range of a million microvolts, 98 per cent. of which would never be used. For thermoelectric work, potentiometers of appropriate range may, in spite of their simplicity, be better adapted

¹ And can easily be introduced by the use of a shunted element (*Instrumentenkunde*, loc. cit.), since with the low range of 18,000 microvolts a single shunted element with a simple switch suffices, and will give an accuracy of .05 microvolt if the switch contact resistance does not exceed .01 ohm.

² *Instrumentenkunde*, loc. cit.

³ By changing the internal connections of a Wolff 20,000 ohm potentiometer, an instrument of constant galvanometer circuit resistance can be made for thermoelectric ranges; the changes involve a rearrangement of the different *groups* of coils without dividing the group, much less touching the individual coils. There is therefore no danger of injury and the instrument can in a very short time be restored to its original condition if that is desired. In making the readjustment the two higher switches are entirely cut out. The compensating coils of the next two decades are changed from the potentiometer circuit proper to the galvanometer circuit; the result is a three-switch instrument of 5,000 instead of 10,000 ohms to the volt, reading up to 19,980 microvolts by steps of 20 instead of 10 microvolts. In dispensing with the two higher switches one terminal of the standard cell must be permanently connected to the potentiometer circuit, but this connection is in itself a decided advantage.

for measurements of the greatest difficulty and refinement than the existing types, while in instruments where less accuracy is required the simplicity can be correspondingly increased.

SUMMARY.

I. For the most accurate pyrometry, with temperatures up to 1600° , the direct reading pyrometer is not sufficiently sensitive, the resistance thermometer has not sufficient range and is, moreover, too bulky for the best melting-point work. A thermoelement with a potentiometer is the most satisfactory measuring apparatus.

II. The most characteristic requirement in melting-point and calorimetric work at high temperatures is rapidity. This is secured : (a) by proper selection and arrangement of the galvanometer. Periods of five seconds are almost necessary and are readily obtained ; (b) by the use of switches to exchange thermoelements, adjust zero, etc., (c) by relying upon the galvanometer for as much of the reading as possible, so as to minimize potentiometer manipulation. For this, constant galvanometer sensibility, and therefore constant resistance in the branch circuit of the potentiometer, is needed. An adjusting rheostat in the circuit secures this result fairly well for ordinary potentiometers, whose branch circuit resistance is variable.

III. External leakage can be absolutely prevented and internal leakage greatly diminished by equipotential shields, which interpose a continuous metallic surface between the circuit and the source of disturbance. Internal leakage also decreases with the resistance of the potentiometer.

IV. The constancy of the potentiometer-storage cell is increased by a wrapping which protects it from temperature changes. For some other minor devices, those interested are referred to the body of the article.

V. With galvanometers of familiar commercial types, a sufficiently short period, five seconds, with satisfactory critical resistance and sensibility, can be obtained with a high resistance potentiometer. Either an especially good galvanometer or potentiometer of low resistance makes possible a somewhat better adjustment.

VI. A slide wire potentiometer is very undesirable in rapid work, and especially in melting-point and calorimetric determinations.

VII. By confining the range of the potentiometer to that actually needed in thermoelectric work, an instrument of almost ideal convenience and usefulness can be obtained at relatively low cost. It has constant galvanometer sensibility, low resistance, and ease of manipulation, and can be used on two circuits alternately without resetting.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
June 3, 1907.

THE THERMOELECTRIC BEHAVIOR OF METALS IN SOLUTIONS OF THEIR OWN SALTS.

II. CADMIUM AMALGAM IN A SOLUTION OF CADMIUM SULPHATE.

BY WILLIAM D. HENDERSON.

INTRODUCTION.

THE present paper is the second in a series on the thermoelectric behavior of metals in solutions of their own salts. Paper I.¹ deals with the thermoelectric behavior of silver. The work herein recorded has to do with the thermoelectric behavior of cadmium amalgam in a solution of cadmium sulphate.

The object of this work is in general, an investigation of the relation of heat to electromotive force. The solution of this problem demands the specific investigation of the thermoelectric behavior of a large number of metals, with respect to the direction and magnitude of the thermoelectromotive force under given conditions, and to the relation of this electromotive force to the concentration of the electrolyte. The problem also involves a study of the subjects of osmotic pressure and solution pressure and allied topics, in so far as these forces play any rôle in the production of an electromotive force.

In pursuing the present investigation three specific objects have been kept in view, as follows: First, to determine the direction of the thermoelectromotive force of cadmium amalgam in a solution of cadmium sulphate; second, to determine the relation between the thermoelectromotive force and the concentration of the electrolyte; and third, to compare the thermoelectromotive force due to a given difference of temperature, with the electromotive force due to a corresponding difference of concentration.

When two electrodes of a given metal are immersed in a neutral solution of a salt of this metal, two causes may operate to produce

¹PHYSICAL REVIEW, Vol. XXIII., 2, August, 1906.

an electromotive force. A difference of temperature at the electrodes will produce an E.M.F., commonly spoken of as a thermo-electromotive force. Also, a difference of concentration of the electrolyte will produce an E.M.F., which for the sake of convenience and clearness is sometimes referred to as a concentration-electromotive force. Whether these two electromotive forces are due to one and the same cause remains to be seen.

The apparatus used was very similar to that employed in the investigation on silver (Paper I.), and is shown in outline in Fig. 1. The letters A_1 and A_2 , as used in the figure, are employed to designate (*a*) the two legs of the cell, (*b*) the electrodes, or (*c*) the electrolyte contained therein.

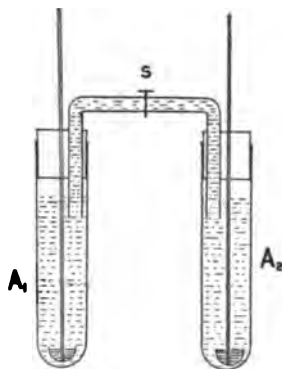


Fig. 1.

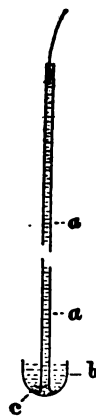


Fig. 2.

The electrodes were prepared as shown in Fig. 2. A glass tube (*a*) was sealed into the bottom of a small glass cup (*b*), about 2 cm. in diameter, and 2.5 cm. in depth. Into the tube (*a*), near the bottom, was sealed a short piece of platinum wire (*c*). Tube (*a*) was then filled with cadmium amalgam. Finally, cup (*b*) after being thoroughly cleaned and dried, was filled with the amalgam under test, after which the entire cell was set up as shown in Fig. 1. The siphon which connects the two legs of the cell was provided with a stopcock (*s*).

Temperatures ranging from 0° to 30° centigrade were employed. The lower temperatures, those near 0°, were obtained by means of crushed ice placed in a large Dewar flask. Those of 25° and 30°

were obtained by means of a thermostat which held constant to within a few hundredths of a degree for days. Beckmann thermometers were used, for the most part.

E.M.F. readings were made by means of an Otto Wolff potentiometer, reading directly to 0.00001 volt.

The electrolyte was prepared by dissolving cadmium sulphate, recrystallized from Kahlbaum's C.P. salt, in water redistilled for conductivity purposes.

The cadmium amalgam was of twelve and one half per cent. strength, prepared by dissolving pure cadmium in redistilled mercury, in the ratio of one part by weight of cadmium to seven parts by weight of mercury.

The method of conducting a test was as follows: A solution of CdSO_4 , or a series of solutions as required, of the desired concentration was prepared as described. Enough amalgam was prepared so that for each test a fresh portion of the amalgam might be used. The electrode cups were cleaned in nitric acid, then washed with distilled water and dried. The amalgam was heated over a water bath until it came to a fluid state, after which the desired amount was transferred to the electrode cups by means of a pipette. The electrodes were then placed in the legs of the cell, and the electrolyte added. The siphon (*s*) was filled, and finally the entire cell adjusted as shown in Fig. 1. At the close of the test the cell was dismantled, and the entire operation then repeated for a new test, as just described.

DIRECTION OF THE THERMOELECTROMOTIVE FORCE.

The object here was to determine the direction of the thermoelectromotive force of a cell of the type, Cd Am. — CdSO_4 — Cd Am., the temperature of electrode A_1 being kept at 0° , and that of A_2 , at 30° . The electrolyte was of the same concentration at both electrodes.

It was observed that cadmium amalgam when placed in a dilute solution of CdSO_4 loses, after a time, its bright metallic appearance, the surface becoming covered with a grayish colored film. It therefore seemed desirable to make a "time test" of a Cd Am. — CdSO_4 thermoelement, to determine how far this film affects the E.M.F.

Two such time tests were made. In the first, a cell of the form shown in Fig. 1 was used. The time was relatively short, readings being taken every ten minutes for an hour and a half. The electrodes A_1 and A_2 were maintained at a difference of temperature ($T_1 - T_2$) of 29.95° . In half an hour the thermoelectromotive force rose to 0.01175 volt, and this value remained unchanged for the following hour, during which readings were taken. Three hours later the cell showed an increase of only 0.00004 volt.

For the second time test a cell similar to that described in detail in Paper I. was set up. A glass tube, about 5 cm. in diameter and 70 cm. in length, sealed off at one end, was filled with a tenth molecular solution of CdSO_4 , and was set up vertically in such a manner that the lower half of the tube was contained in an ice bath, and the upper half in a water bath at 30° . One electrode was placed at the bottom of the cell, the other at the top. The difference of temperature of the electrodes was, therefore, equal to the difference of temperature between the ice bath and the water bath.

This test extended over a period of ten days. The results, as tabulated in Table I., show (a) that the E.M.F. is directed, in the external circuit, from the warm electrode to the cold — that is, the warm electrode is the cathode; and (b) the E.M.F. increases slightly with the time, due probably to the film mentioned. It must be noted, however, that this increase, over a period of ten days, was only 0.00033 volt.

TABLE I.

Time in Hours.	$T_1 - T_2$.	E.M.F. in Volts.	Time in Hours.	$T_1 - T_2$.	E.M.F. in Volts.
0	30.00°	0.00006	106	29.96°	1173
27	30.00	0.01162	118	29.99	1174
32	30.00	1163	123	30.02	1175
37	30.00	1162	142	29.98	1173
47	30.00	1163	154	29.96	1175
58	30.00	1164	174	30.00	1179
75	30.00	1172	192	29.95	1183
80	29.97	1173	214	29.95	1182
94	29.96	1172	220	29.96	1194
99	30.01	1176	244	29.96	1195

RELATION OF THE THERMOELECTROMOTIVE FORCE TO THE CONCENTRATION OF THE ELECTROLYTE.

For this test a series of solutions was prepared having the following concentrations: $n/80$, $n/40$, $n/20$, $n/10$, $n/5$. A normal solution as here used, means a gram molecule of the salt dissolved in one liter of water. The method pursued was as follows: The electrode cups (*b*, Fig. 2) were filled with cadmium amalgam, and then adjusted in the cell, as previously described. The eightieth normal solution ($n/80$) was used first. Electrode A_1 was placed in the ice bath; and A_2 in the 30° bath. The E.M.F. rapidly rose to a constant value, which was recorded.

The electrolyte was now removed and the cell washed and dried. The amalgam was also removed from the electrode cups, which were cleaned and dried, after which a fresh portion of the amalgam was added. A solution of the next higher concentration was then tested.

TABLE II.

Con.	$n/80$	$n/40$	$n/20$	$n/10$	$n/5$
T. E. M. F.	0.01024	0.01070	0.01107	0.01142	0.01172
"	1040	1081	1116	1148	1176
"	1029	1080	1111	1148	1175
"	1028	1083	1111	—	1173

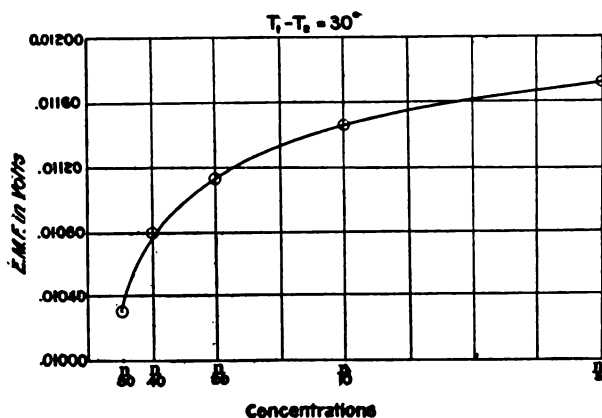


Fig. 3.

Four series of readings were made, a record of which is given in Table II., and the corresponding curve in Fig. 3. Table II., which

shows an excellent agreement between the E.M.F. readings, indicates, together with the curve of Fig. 3, that the thermoelectromotive force *increases* with the concentration of the electrolyte.

COMPARISON OF THE E.M.F. DUE TO A GIVEN DIFFERENCE OF
ABSOLUTE TEMPERATURE, WITH THE E.M.F. DUE TO A
CORRESPONDING DIFFERENCE OF CONCENTRATION.

The object and conditions of the experiment were as follows: The entire cell was filled with a given solution, $n/10$ say, and the electrodes subjected to a difference of temperature of 30° , which produced a given E.M.F. The ratio of T_2/T_1 , measured on the absolute scale, was therefore, in this case equal to $303/273 = 1.11$.

Now it was desired to find what E.M.F., would be produced by a corresponding concentration ratio—that is $C_2/C_1 = 1.11$, the temperature of both electrodes being the same. To obtain the electromotive force due to this concentration ratio it was determined to plot two E.M.F. curves, obtained by different methods, such that one would serve as a check on the other. The two methods of procedure and the results are given in the following paragraph.

First Method.—A series of solutions of CdSO_4 was prepared, having the following concentrations: $5n/100$, $8n/100$, $10n/100$, $12n/100$, $15n/100$, $20n/100$. These particular concentrations were chosen, (a) because they gave a range which included the tenth molecular solution selected as a standard, and (b) because accurately calibrated pipettes capable of producing this series, were available.

One leg of the cell was filled with $10n/100$ solution and placed in the 30° bath. The concentration of this solution was unchanged throughout the experiment. The other leg of the cell was placed in the ice bath. The concentration of the electrolyte in this (the cold) portion of the cell was varied from $5n/100$ to $20n/100$.

To begin with, the E.M.F. of the cell was directed, in the external circuit, from the warm electrode to the cold electrode. It is evident therefore that the effect of increasing the concentration at the cold electrode would be to produce a counter E.M.F., which at a certain point would just balance the thermoelectromotive force. It is evident, also that the cell was operated both as a thermoelement and a concentration element at the same time, except at the

point at which the concentration at both electrodes became the same ($n/10$), at which instant the cell was functioning as a thermoelement only.

A record of the experiment is contained in Table III.

TABLE III.

$T_1 - T_2$	C. of Warm El.	C. of Cold El.	E.M.F.
30.02	10n/100	5n/100	0.01690
30.01	"	8/100	1352
30.02	"	10/100	1187
29.98	"	12/100	1072
30.00	"	15/100	905
30.00	"	20/100	738

Second Method.— The experiment was now repeated, though in a somewhat modified form, in order to obtain a second E.M.F. curve to serve as a check on the first.

The entire cell was placed in the 30° bath, both electrodes being therefore at the same temperature. The concentration of the electrolyte A_1 was held at 10n/100 throughout the experiment. The concentration of A_2 was varied from 5n/100 to 20n/100 as before. In this case the element was operated purely as a concentration cell.

The results of this series of tests are given in Table IV.

TABLE IV.

$T_1 - T_2$	C. of A_1 .	C. of A_2 .	E.M.F.
0.0	10n/100	5n/100	+0.00540
0.0	"	8/100	246
0.0	"	10/100	4
0.0	"	12/100	-0.00104
0.0	"	15/100	291
0.0	"	20/100	460

If now the concentrations be plotted as abscissas and the E.M.F. readings as ordinates, Tables III. and IV. give a pair of E.M.F. curves which theoretically should coincide when drawn with reference to x -axes 1,187 units apart.

Fig. 4 shows such a combination of E.M.F. curves. The continuous line represents E.M.F. readings due to both a difference of

temperature and concentration, as given in Table III. The curve represented by the broken line is taken from the data given in Table

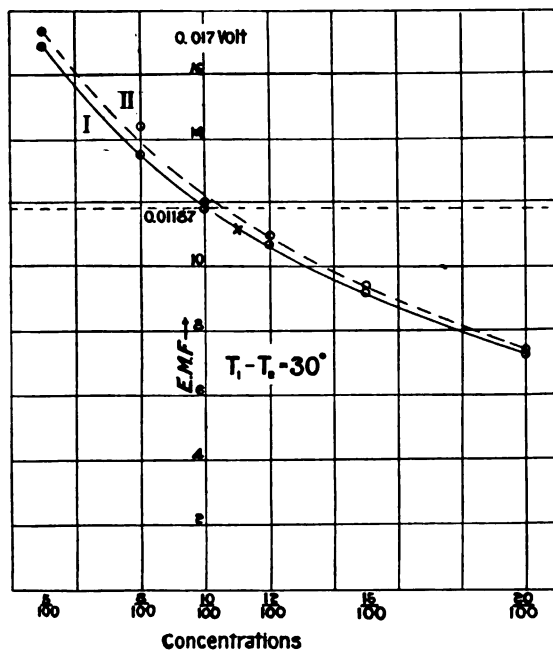


Fig. 4.

IV., and is drawn with reference to the x -axis indicated by the horizontal dotted line.

The point (x) on curve I is the point at which the concentration ratio $C_2/C_1 = 1.11$ might be expected to produce an E.M.F. equal to that resulting from the absolute temperature ratio, $T_2/T_1 = 1.11$.

It will be noted, however, that there is at this point on the curve an outstanding E.M.F. of over 0.01100 volt. That is to say, a difference of concentration represented by the ratio $C_2/C_1 = 1.11$ will produce an E.M.F. equal to 0.00128 volt; while, on the other hand, corresponding difference of absolute temperature ($T_2/T_1 = 1.11$) will produce an E.M.F. equal to 0.01187 volt, a value nearly ten times as great.

SUMMARY.

1. Cadmium amalgam in a solution of cadmium sulphate gives between 0° and 30° , a thermoelectromotive force directed, in the

external circuit, from the warm electrode to the cold—that is, the warm electrode in the cathode. It was shown in Paper I. that in the case of silver the conditions are just the opposite, the *cold* electrode being the cathode. Further, with cadmium amalgam, the thermoelectromotive force is relatively constant, and for given concentrations is reproducible.

2. The thermoelectromotive force is a function not only of the temperature but also of the concentration of the electrolyte, an increase in concentration producing an increase of E.M.F. In the case of silver, the conditions are again reversed, an increase in concentration of the electrolyte producing a decrease of E.M.F.

3. Within a range of temperature from 0° to 30° , the thermoelectromotive force due to a given difference of absolute temperature is nearly ten times as great as the E.M.F. due to a corresponding difference of concentration. It therefore follows that the thermoelectromotive force observed cannot be accounted for on the assumption of an increase of osmotic pressure, since according to the theory a given increase of osmotic pressure due to a given difference of absolute temperature should be equal to that due to a corresponding difference of concentration. Nor can we well assign the large outstanding E.M.F., shown in Fig. 4, to a change of solution tension in the cadmium amalgam, unless we are willing to assume, since the warm electrode is the cathode, that the solution pressure of the metal *decreases* with an *increase of temperature*.

UNIVERSITY OF MICHIGAN,
May 20, 1907.

STUDIES IN LUMINESCENCE.

BY EDWARD L. NICHOLS AND ERNEST MERRITT.

VIII. THE INFLUENCE OF THE RED AND INFRA-RED RAYS UPON
THE PHOTOLUMINESCENCE OF SIDOT BLENDE.

THE effect of the red and infra-red rays in suppressing the phosphorescence of various substances has long been known,¹ and has frequently been utilized in the study of the infra-red spectrum. The effect is exhibited by Sidot blende more strongly perhaps than by any of the other phosphorescent sulphides. In the preceding paper of this series² we have called attention to another effect produced by the longer waves, namely the restoration of a screen of Sidot blende, after the excitation and complete decay of phosphorescence, to a standard condition, so that the result of a subsequent excitation shall be unaffected by the previous history of the substance. While this new effect is doubtless connected in some way with that first mentioned, the nature of the relationship between the two is by no means clear. For this reason, and because of the bearing of the phenomena upon the general theory of luminescence, we have investigated the influence of the longer waves upon the luminescence of Sidot blende under a variety of different conditions. The experiments to be described in the present paper were made during the progress of work upon the luminescence of Sidot blende that has already been published, and have extended over a period of about three years. While there are certain parts of the work where additional investigation is much to be desired, it has seemed inadvisable to postpone longer the publication of the results thus far obtained, since the experimental work has been interrupted and cannot be taken up again for some months.

¹ References to the literature of the subject are given by Dahms, *Annalen der Physik*, Vol 13, p. 425.

² Further Experiments on the Decay of Phosphorescence, *PHYSICAL REVIEW*, Vol. 23, p. 37, 1906.

The work naturally falls under several heads as follows :

1. The effect upon the luminescence of Sidot blende of exposure to the longer waves *before* excitation.
2. The effect of the longer waves *during* excitation.
3. The effect of the longer waves *after* excitation, *i. e.*, during the decay of phosphorescence.
4. The influence upon the effect studied of the wave-length of the red and infra-red rays used.

1. THE EFFECT OF THE LONGER WAVES BEFORE EXCITATION.

Experiments described in the preceding paper of this series have shown that when Sidot blende is excited to luminescence "some change is produced in the material by the action of the exciting light, and that this change persists for a considerable period after all visible phosphorescence has ceased. In other words the effect of a given excitation in producing phosphorescence depends upon the previous history of the phosphorescent substance. If the screen is allowed to rest in the dark for a number of hours this semi-perma-

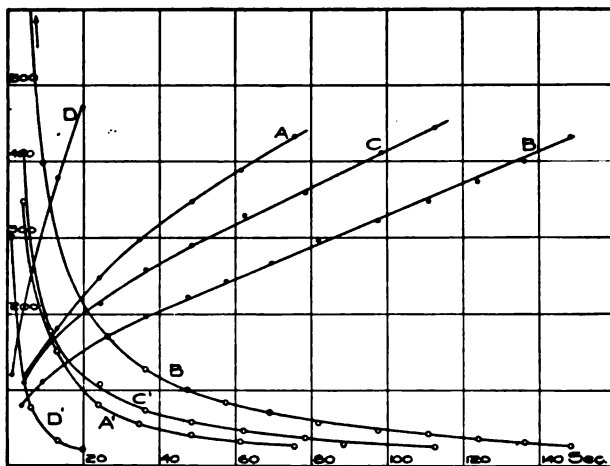


Fig. 42. Illustrating the relative effect of rest and of exposure to infra-red.

A, 10 sec. excitation after rest of 24 hours in the dark.

B, 2 min. excitation.

C, 10 sec. excitation immediately after B.

D, 10 sec. excitation after exposure of 4 min. to infra-red from 50 candle power lamp

Curves A', B', C', D' correspond to A, B, C, D except that I is plotted in place of $I - \frac{1}{2}$.

ment effect of exposure in part dies out. But rest alone does not restore the screen completely even if continued for several days." An exposure of a few seconds to the rays from a 50 c.p. lamp seen through ruby glass is however sufficient to restore the screen to what seems to be a definite standard condition.

The phenomenon in question is well illustrated by the curves of Fig. 42, which is reproduced from our last article. If we compare curves *A*, *C* and *D*, all corresponding to the same excitation, it is clear that exposure to the longer waves *before* excitation exerts a very marked influence upon the rate at which the phosphorescence, excited after this exposure, will decay. While the semi-permanent change produced by excitation is partly lost as the result of prolonged rest in the dark, rest alone is not a very satisfactory means of restoring the substance to a standard condition. Thus a rest of 24 hours brings about a change in the decay curve following a 10-sec. excitation from *C* to *A*. Rest for several days would shift the curve somewhat further to the left. But even a rest of several weeks failed to bring the decay curve as far to the left as curve *D*.

Curve *D*, Fig. 42, was taken after an exposure of four minutes to the longer waves. A very much shorter exposure would have been

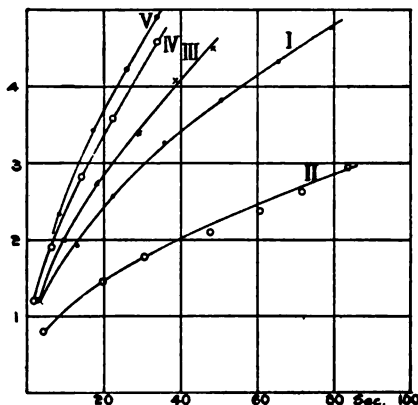


Fig. 55. Effect on the decay curve of exposure to the infra-red for different times.
 Curve I. 10 sec. exposure after 48 hrs. rest in the dark.
 Curve II. 2 min. exposure.
 Curve III. 10 sec. exposure after 1 sec. infra-red.
 Curve IV. 10 sec. exposure after 3 sec. infra-red.
 Curve V. 10 sec. exposure after 60 sec. infra-red.

nearly, if not quite, as effective. This point is brought out by the curves of Fig. 55, which were taken to determine the way in which the effect depended upon the duration of exposure to the longer waves. In taking these curves the procedure was as follows: In each case the screen was first exposed for two minutes to the mercury arc; the phosphorescence was then allowed to decay for two minutes, at the end of which time, while still visible, it was too faint for measurement. The screen was then exposed to the rays of a 50 c.p. lamp at a distance of 5 inches, a piece of ruby glass being interposed between the lamp and the screen; the duration of this exposure was 1 sec. for Curve III., 3 sec. for Curve IV., and 60 sec. for Curve V. After this exposure to the longer waves the screen was excited by the mercury arc for 10 sec., and the decay curves shown in Fig. 55 were observed by the procedure described in our last paper.

It will be observed that even an exposure of only 1 sec. is more effective than 48 hours' rest. It will be noticed also that 3 sec. exposure to the longer waves is nearly as effective as an exposure of a minute.

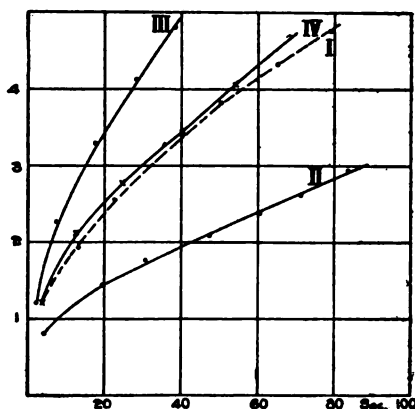


Fig. 56. Effect on the decay curve of exposure to the infra-red for different times. The intensity of the infra-red rays was here only about $\frac{1}{8}$ of the intensity used for the curves of Fig. 55.

Curve I. 10 sec. exposure after 48 hrs. rest in the dark.

Curve II. 2 min. exposure.

Curve III. 10 sec. exposure after 60 sec. infra-red.

Curve IV. 10 sec. exposure after 15 sec. infra-red.

With red and infra-red rays of less intensity a longer time is required to destroy the effect of previous excitation. The curves of

Fig. 56 were taken with a procedure similar to that for Fig. 55, except that the distance of the 50 c.p. lamp from the Sidot blende screen was 30 inches instead of 5 inches. Exposure for 60 seconds to these less intense rays produces as great an effect as a similar exposure to the stronger rays. But this is not true for shorter exposures. While the ultimate effect of the weaker rays is apparently the same, more time is required to produce the change when the rays are of small intensity; approximately, at least, the change produced depends upon the product of intensity and duration of exposure.

The experimental data bearing upon this phase of the subject are so meager as to permit of only the most general conclusions, and additional experiments are much to be desired. So far as they go however the results indicate that the condition in which the material is left after the excitation and decay of phosphorescence is an unstable one, due perhaps to some new grouping of the molecules of the phosphorescent material. During rest in the dark accidental disturbances of various kinds may cause the substance to return more or less completely to its normal condition. The effect of rest is therefore uncertain, depending as it does upon the extent to which various obscure and perhaps unrecognized agencies are active. Certain waves, however, lying chiefly in the infra-red region of the spectrum, have a definite and positive effect in restoring the substance to its normal condition.

INFLUENCE OF THE LONGER WAVES DURING EXCITATION.

We have seen that a condition is developed in Sidot blende by excitation which is favorable to the production of strong luminescence by a subsequent excitation. A long excitation is therefore more effective than exposure to equally intense exciting rays for a shorter period; for the favorable condition developed in the early stages of excitation makes the exciting rays that act later more effective. The luminescence of such a substance during excitation — *i. e.*, the fluorescence — will be relatively weak when excitation first begins and will increase in intensity as the exposure continues, reaching a steady value only after a considerable time. In Sidot blende, with the exciting light used in most of our experiments, three or four minutes were required to reach a steady value.¹

¹ See the preceding paper of this series, *l. c.*

The steady condition finally reached is manifestly characterized by equality in the rates of development and decay of the condition favorable to luminescence to which we have just referred. If we think of this favorable condition as being due to some new grouping of the molecules, then the condition of steady fluorescence is reached when these favorable groups are being broken up, either spontaneously or through the action of some outside agent, just as rapidly as they are formed by the action of the exciting light.

It is clear that the intensity of steady fluorescence will be made less by any agent which increases the rate at which the assumed favorable grouping is destroyed. Now it is precisely this effect that is exerted by the red and infra-red rays; and we should therefore anticipate that the fluorescence of Sidot blende would be diminished by the action of the longer rays.

This effect of the longer waves, which does not appear to have attracted much attention heretofore, may readily be made very marked indeed. Thus the rays from a projecting lantern after passing through a sheet of hard rubber 0.2 mm. thick are able to reduce the fluorescence of Sidot blende so greatly as to leave the intensity only a few per cent. of its normal value, and this too with very intense excitation. If the ultra-violet rays of a spark are used for excitation numerous lecture experiments may be devised for demonstrating the existence of the invisible rays at the two ends of the spectrum. As compared with the experiments first proposed by Dahms, in which the effect of the infra-red rays upon phosphorescence is utilized, this procedure has the advantage of giving a persistent rather than a fleeting effect.

In studying the influence of the longer rays upon fluorescence we have directed our attention especially to the distribution of the effect throughout the fluorescence spectrum. While the result of exposure to longer waves is to unquestionably diminish greatly the *total* brightness of the fluorescence light, it might be that in certain restricted regions of the spectrum the intensity would be increased rather than diminished, or at least that the effect of the infra-red rays would vary greatly in magnitude in different parts of the fluorescence spectrum.

For the work on this phase of the subject the Sidot blende screen

was mounted in front of a Lummer-Brodhun spectrophotometer, with an acetylene flame as a comparison source as in our previous work. The infra-red rays from an arc fell upon the screen after passing

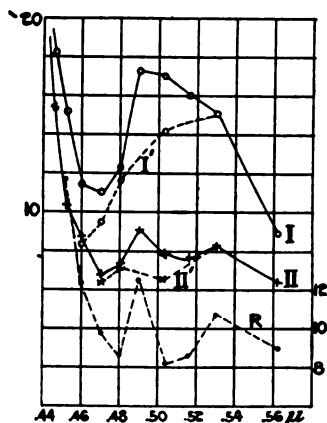


Fig. 57. Effect of infra-red on fluorescence. Sidot blend excited by "uviol" mercury vapor lamp.

Curve I. Fluorescence spectrum.

Curve II. Fluorescence spectrum when the screen is exposed to infra-red during excitation.

Curve I.' Fluorescence spectrum with plate glass between screen and mercury lamp.

Curve II.' Same as I.' except that screen is also exposed to infra-red.

Curve R. Reflection of exciting light from white surface.

through hard rubber. The intensity of fluorescence was then measured in different parts of the spectrum, first with, and then without the action of the longer waves, the excitation remaining constant. As exciting source a mercury vapor lamp was first used, the lamp being made of the so called "Uviol" glass, which possesses an unusual transparency to the ultra-violet rays.

In Fig. 57, Curve I. shows the ordinary fluorescence spectrum of Sidot blende produced by the mercury lamp, while Curve II. shows the spectrum as modified by exposure to the infra-red. In the case of Curves I.' and II.' a sheet of ordinary glass was interposed between the lamp and the screen, so that the ultra-violet rays were in large part removed from the exciting light. It is clear that the ultra-

violet-rays of the Uviol lamp introduce a band at about $.49 \mu$ which overlaps and distorts in an annoying way the usual green band at 0.51μ .

A more annoying source of disturbance in these experiments, however, was the light reflected from the screen, which was mixed with fluorescence light and practically inseparable from it. By making observations only at points lying between the bright lines of the mercury spectrum we had expected to be untroubled by reflected light. But owing either to optical imperfections in the apparatus or to the existence of a faint continuous spectrum in the light from the lamp, there was always enough reflected light in the field of

the spectrophotometer to be an important and disturbing factor. To get some idea of the intensity and distribution of this reflected light we made the observations plotted as Curve *R* in Fig. 57 with a screen of MgO on cardboard instead of the Sidot blende screen. To avoid confusion this curve is displaced downward in the plot. The intensity for points on Curve *R* should be read from the right hand side of the figure.

The irregular distribution of the reflected light and the great uncertainty in its measurement make the experiments plotted in Fig. 57 of little quantitative value. Especially is this true for the violet end of the spectrum, where the reflected rays are of great intensity. We could not even feel sure that the longer waves produced any effect at all in this region.

With a different zinc sulphide screen, the so called "Emanations pulver" referred to in the foregoing paper of this series, the conditions were somewhat more favorable. The curves in Fig. 58 show the ordinary fluorescence spectrum (Curve I.); the fluorescence spectrum with exposure to weak infra-red rays

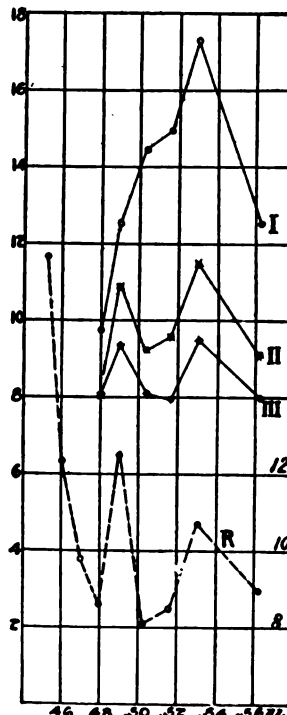


Fig. 58. Effect of infra-red on the fluorescence of "Emanationspulver," excited by the uviol lamp.

(Curve II.); the fluorescence spectrum during exposure to strong infra-red rays (Curve III.); and the reflected light determined as before. Different intensities of infra-red were obtained by using in one case one piece of black rubber and in the other case two pieces between the arc lamp and the screen. By this procedure it is possible to determine the *ratio* of the effects produced by strong and weak infra-red, in spite of the uncertainty in the value of the reflected light. Thus the difference between the ordinate of Curve I. and the corresponding ordinate of Curve II. is a measure of the effect produced by weak infra-red; reflected light, since it affects

both measurements, is eliminated by taking their difference. Similarly the difference between the ordinates of Curves II. and III. measures the effect of the stronger infra-red. It is interesting to note that the ratio of these effects is nearly constant throughout the green band. Beginning at $0.562\ \mu$ and running toward the violet the ratio has the values: 1.32, 1.36, 1.31, 1.22, 1.94. Except for the last point, which is so near the edge of the band that the intensity of fluorescence is small, the values are constant to within observational

errors. This fact adds another to the many that have been observed in the course of our work on luminescence to indicate that each band in a luminescence spectrum behaves as a unit — that whatever affects one part of the band affects all other parts of the band in the same proportion.

In some ways the most satisfactory method of studying the effect in question is to use only ultra-violet light in excitation. All troubles due to reflected light are in this case removed. The results of this procedure in the case of the original Sidot blende screen used in our earlier experiments are shown in Fig. 59. An iron spark was used as an exciting source, a spectrum being formed by a

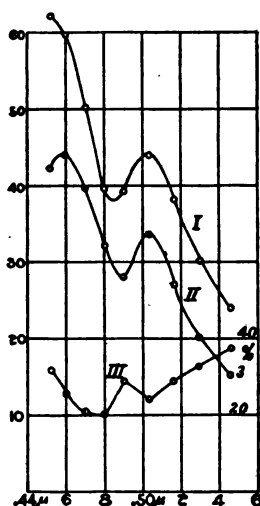


Fig. 59. Effect of infra-red upon the fluorescence of "Emanationspulver" excited by the ultra-violet rays of an iron spark.

quartz train and only the ultra-violet rays used. The source of infra-red was an arc lantern whose rays passed through a sheet of hard rubber 0.2 mm. thick. The effect of exposure to longer rays during excitation by the ultra-violet rays of the iron spark was to change the fluorescence spectrum from Curve I. to Curve II. The diminution in intensity brought about by exposure to the longer rays, expressed as a fraction of the ordinary fluorescence at the same wave-length, is given in Curve III.

More extended experiments are required to determine whether the change in the effect from 38 per cent. at $0.546\ \mu$ to 20 per cent. at $0.480\ \mu$ is real, or the result of errors. It does not seem likely,

however, that experimental errors alone can account for so great a change. In interpreting the results we must bear in mind the fact that the spectrum shown in Fig. 59 obviously consists of two overlapping bands, and that the infra-red effect may differ for the two. It is highly probable also that still another band is present at $0.49\ \mu$, as was found to be the case with ultra-violet excitation in the experiments plotted in Fig. 57; and for this band the effect of the longer waves may be different still. It is clear that further experiments on this branch of the subject are needed.

EFFECT OF THE LONGER WAVES DURING DECAY.

In studying the effect of the infra-red rays upon the decay of phosphorescence two methods were used. In the first of these the intensity of the total phosphorescent light was measured by a photometer at different times after excitation had ceased, by the same procedure as that described in our last article. The violet end of

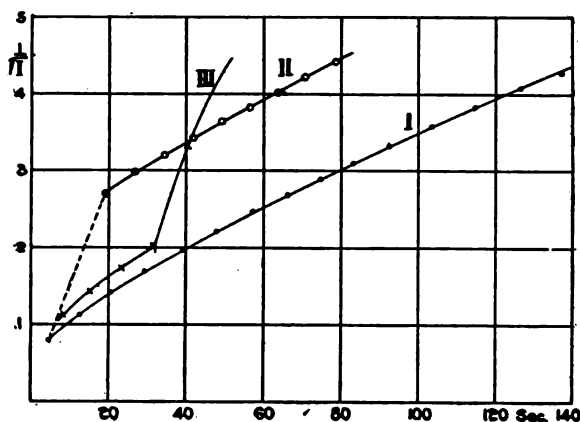


Fig. 60. Influence of exposure to infra-red during decay upon the form of the decay curve.

Curve I. Ordinary decay curve.

Curve II. Screen exposed to infra-red after decay had proceeded for 4 sec. Infra-red cut off at $t = 19$ sec.

Curve III. Screen exposed to infra-red after decay had proceeded for 32 sec.

the carbon arc spectrum was used for excitation, and a 50 c.p. incandescent lamp as a source of infra-red rays. In these experiments a cell containing a solution of iodine in carbon disulphide was used

instead of hard rubber to remove the visible rays. The distance of the lamp from the Sidot blende screen was about 60 cm.

The curves of Figs. 60 and 61 show some of the results obtained by this procedure. In Fig. 60, Curve I. is the ordinary decay curve without exposure to infra-red. In the case of Curve III. the infra-red rays were allowed to fall on the screen when the decay

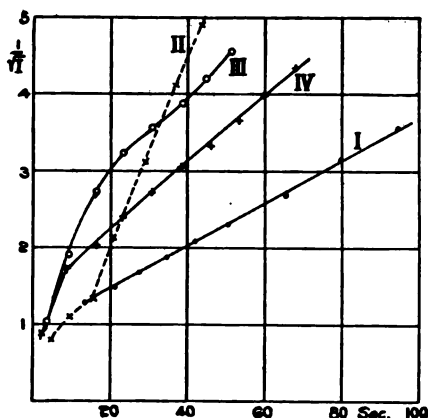


Fig. 61. Influence of exposure to infra-red during decay upon the form of the decay curve.

Curve I. Ordinary decay curve.

Curve II. Screen exposed to infra-red after the decay had proceeded for 18 sec.

Curve III. Screen exposed to infra-red during excitation and for the first 16 sec. of decay.

Curve IV. Screen exposed to infra-red during excitation and for the first 9 sec. of decay.

had proceeded for about 32 sec. In Curve II. the infra-red rays were turned on about 4 sec. after the end of excitation and were cut off again at the end of about 19 sec. The great increase in the rapidity of decay brought about by infra-red rays, even when of such small intensity as those used in these experiments, is clearly shown.

There was no indication in these experiments of any temporary *increase* in the brightness of phosphorescence when the rays were first turned on, as has been noted by many observers in the case of Balmain's paint and other phosphorescent sulphides. Dahms has already called attention to this peculiarity of Sidot blende. The effect of the longer waves in suppressing phosphorescence has sometimes been explained by assuming that these rays act in the same

way as does a rise of temperature; *i. e.*, that they accelerate the process which causes phosphorescence, so as to produce a brief flash, due to the sudden liberation of the energy stored during excitation, followed by a complete loss of luminescence when the stored energy has been used up. While this explanation of the phenomenon may be correct for the other phosphorescent substances it cannot be applied without essential modification to the case of Sidot blende.

Perhaps the most striking feature of the curves in Fig. 60 is the nearly exact parallelism that exists between the later part of Curve III. (after the infra-red rays were cut off) and the straight part of the ordinary decay curve. The action of the longer waves appears to be to bring the material quickly into the same condition as regards ability to emit light that it would have acquired at the end of a much longer period of ordinary decay.

In the case of Curves III. and IV. of Fig. 61 the screen was exposed to infra-red during excitation and during the early stages of decay. The infra-red rays were cut off at the points indicated by the break in the curves. It will be noticed that the latter portion of Curve III. is nearly parallel to the straight part of the ordinary decay curve; but in Curve IV., where the infra-red was cut off earlier, the straight part of the curve is not even approximately parallel to Curve I.

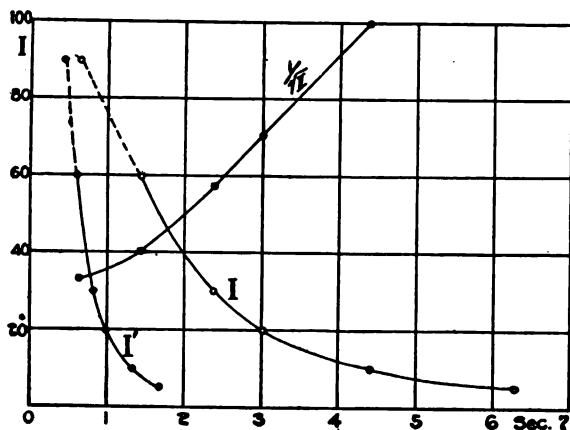


Fig. 62. Influence of exposure to infra-red on form of decay curve.

Curve I. Ordinary decay curve for $\lambda \times 0.497 \mu$.

Curve II. Screen exposed to infra-red immediately after the end of excitation.

For the early stages of decay a number of curves were taken by means of the spectrophotometer, the method being that described in the fifth and sixth papers of this series.¹ With this method it is impracticable to follow the decay for more than a few seconds, since the illumination of the spectrophotometer field soon becomes too faint for accurate measurements. The method possesses a great advantage, however, in the fact that the effect of the long waves can be determined for different parts of the phosphorescence spectrum.

For the curves shown in Figs. 62 and 63 the exciting light was

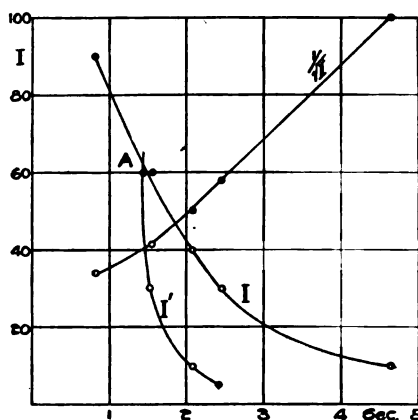


Fig. 63. Curve I. Ordinary decay curve for $\lambda \times 0.497 \mu$.

Curve II. Screen exposed to infra-red after decay had proceeded to A.

the violet of the carbon arc spectrum. For the curves of Figs. 64–67 a spark between cadmium terminals was used in excitation. The intensity of phosphorescence has been plotted in all of these curves instead of the reciprocal square root, although in some cases the latter value has been plotted also. In all these figures the curve marked I. was taken without infra-red² and that marked I.' with infra-red. In general the exposure to infra-red began at the instant the excitation ceased, the shutter being arranged so that the same movement that cut off the exciting rays allowed the infra-red rays to fall upon

¹ PHYSICAL REVIEW, Vol. XXI., p. 247; and Vol. XXII., p. 279.

² The carbon arc was used as a source of infra-red, a piece of dense ruby glass serving as a filter. Red light, and perhaps a little yellow light, was therefore present in addition to the infra-red. There has been nothing in our experiments to indicate that the presence of these visible rays modifies the results in any way.

the screen. In the case of Fig. 63 exposure to the infra-red did not begin until about 1.4 sec. after the end of excitation. Numerous

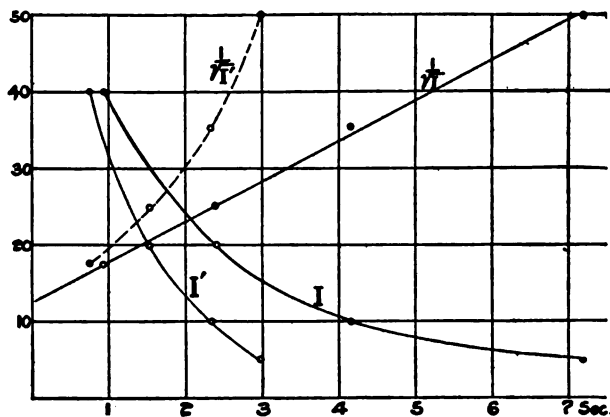


Fig. 64. Decay curves with and without infra-red. $\lambda = 0.546\mu$.

curves of this kind were taken in which the exposure to infra-red began at different times after the beginning of decay. All of these

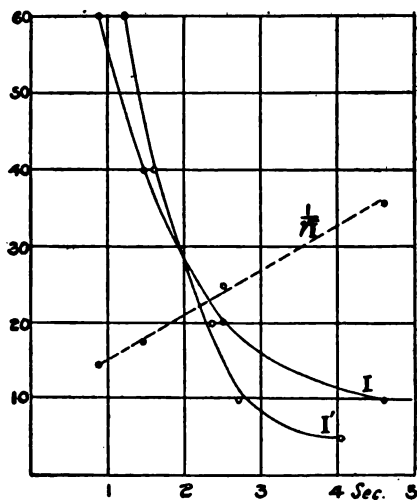


Fig. 65. Decay curves with and without infra-red. $\lambda = 0.474\mu$.

curves show the same sudden drop in intensity at the instant that the long waves begin to act.

The curves of Figs. 62, 63, and 64, except for the method of

plotting, are quite similar to the curves for the total light obtained by the photometer method first described. Apparently the action of the longer waves during the first few seconds of decay is quite similar to its action later. It will be observed that the curves of Figs. 62-64 refer to regions of the phosphorescence spectrum either near the maximum or toward the red edge of the band.

Figs. 65, 66 and 67 show the influence of the longer waves upon those regions of the fluorescence spectrum lying near and beyond the violet edge of the green band. Here the effect seems to be entirely different. At $0.445\ \mu$ (Fig. 67) the effect of exposure to infra-red is to retard the decay of phosphorescence instead of to accelerate it. In the region lying between the green band ($0.51\ \mu$) and the violet band ($0.45\ \mu$) the effect of the infra-red is at first to retard the decay and later to accelerate it (Figs. 65 and 66).

Owing to the faintness of the spectrophotometer field and the rapidity with which the phosphorescence decays it is difficult to determine the form of the curves in the early stages of decay with accuracy. Especially is this true in the blue and violet, owing to the small luminosity of this region of the spectrum. Each point plotted represents however the average of a number of separate readings. For each pair of points the observations for the time of decay with and without infra-red were taken alternately. No special precautions were taken to keep the exciting source constant. The slight initial curvature of the line for I^{-1} in Figs. 62 and 63, where the exciting light was from the carbon arc is perhaps to be explained as the result of variations in this source. In the case of the other observations, in which a spark was used in excitation, the points for I^{-1} lie reasonably well upon a straight line, and thus give a check upon the accuracy of the observations.

The remarkable reversal in the effect of infra-red in passing through the luminescence spectrum received ample qualitative confirmation. With the spectrophotometer set for some region in the blue or violet the brightness of the field increased noticeably for a few seconds when the screen was exposed to infra-red during decay, even when the exposure first began several seconds after the end of excitation. The same effect was observed in the case of "emana-tions pulver" and Balmain's paint. In the case of the latter sub-

stance the flash that accompanied exposure to the longer waves developed more slowly and lasted longer than in the case of Sidot blende.

Two interpretations of the results brought out in Figs. 62–67 suggest themselves. Neither, however, is wholly satisfactory.

In all of these experiments the luminescence spectrum consisted of two bands, namely, the green band at $0.51\ \mu$, and the violet band at about $0.45\ \mu$. It is possible that the infra-red rays retard the decay of phosphorescence in the case of the violet band and accelerate it in the case of the green band. In the curves of Fig. 67 we

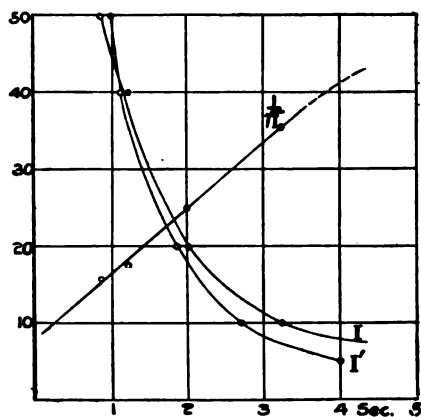


Fig. 66.

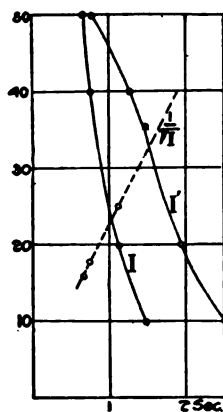


Fig. 67.

Decay curves with and without infra-red. $\lambda = 0.464\ \mu$ (Fig. 66) and $\lambda = 0.445\ \mu$ (Fig. 67).

are dealing with the violet band only; in Figs. 62, 63 and 64 the light is almost entirely from the green band; but at wave-lengths $0.474\ \mu$ (Fig. 65) and $0.464\ \mu$ (Fig. 66) the light entering the collimator slit must be partly from one of these bands and partly from the other. The violet band apparently decays more rapidly than the green band. (Compare the slant of the line for I^{-t} in Fig. 67 and Fig. 64.) If the violet band is initially the brighter of the two the retarding effect of the infra-red upon the decay of this band will predominate in the early stages of decay; while later, when the violet band has nearly died out and the light is chiefly due to the green band, the opposite effect will predominate. The two curves I. and I' will therefore intersect, as shown in Fig. 65 and Fig. 66.

Two objections may be urged to this explanation. If the light in the case of Figs. 65 and 66 is from two bands that decay at different rates we should hardly expect the relation between t and I^{-1} to be as simple as the linear relation that holds for the green band alone. Yet the deviation from a linear relation in both these cases is well within the errors of observation. Again, if the infra-red rays increase the brightness of the violet band after excitation has ceased it would seem reasonable to expect a similar effect during excitation. Yet the effect during excitation (Fig. 59) is practically the same for both bands.

We were first led to expect increased brightness in the violet during exposure to the infra-red, and to undertake experiments in the hope of detecting such an effect, as the result of an entirely different line of reasoning. Looking upon phosphorescence as due to the recombination of ions dissociated by the action of the exciting light, we have explained the fact that the phosphorescence light is of greater wave-length than the exciting light (Stokes' Law) briefly as follows: Dissociation results from the violent resonant vibration of a neutral molecule of the active substance under the influence of the exciting waves. The wave-lengths of maximum resonance and therefore maximum excitation is determined by the natural period of vibration of the active molecule, which is influenced to some extent, but not greatly, by the surrounding solvent. The charged ions resulting from excitation will however be attracted by the neutral molecules of the solvent and will form the nuclei of heavy aggregations of molecules; and recombinations of the ions will therefore occur under conditions which make the resulting vibrations longer, on the whole, than the period of the active molecules before dissociation. Hence the well-known displacement of the luminescence spectrum with reference to the absorption spectrum.

Now the effect of the infra-red rays may be to so shake up the molecules of the solvent as to prevent the loading down of the ions by the attraction of neutral molecules, or to destroy such heavy aggregations if already formed. Under the influence of the infra-red therefore the light emitted will be due largely to the vibrations that occur during the recombination of *unloaded* ions and will be of the same wave-length as that which the active substance absorbs.

If the screen is exposed to infra-red rays after excitation we should expect a decrease in the intensity of phosphorescence throughout the phosphorescence band due to the breaking down of the groups of molecules referred to above. But owing to the resulting increase in the number of unloaded ions we should also expect the emission of light whose wave-length is that of the resonant absorption band of the substance. Now the absorption band always lies on the ultra side of the luminescence band, and usually the two bands overlap. (That this is the case with Sidot blende is evidenced by the fact that this is one of the substances for which Stokes' Law, in its strict form, is violated.) Exposure to infra-red should therefore produce increased intensity near and beyond the violet edge of the phosphorescence band ; which is exactly what we have observed.

In the region where the absorption and emission spectra overlap, the effect will be more complicated. While the light in this region due to the ordinary luminescence band will diminish, there will be at the same time a temporarily increased emission due to the recombination of the unloaded ions that are shaken loose by the infra-red vibrations. A bright flash immediately after the exposure to infra-red followed by decay more rapid than the normal, is therefore to be expected in the intermediate region corresponding to Figs. 65 and 66.

The effect of the longer waves during excitation (Fig. 59) is unfortunately as hard to reconcile with this explanation of the phenomena as with that first suggested. It seems on the whole preferable to wait until additional data have been accumulated and other substances studied before attempting to develop the theoretical side of this extremely puzzling subject.

VARIATIONS OF THE EFFECT WITH THE WAVE-LENGTH OF THE LONGER WAVES.

In the case of several phosphorescent substances, including Sidot blende, the effect of rays of different wave-length in suppressing phosphorescence has been studied by a photographic method of Dahms. Our own results, obtained by an entirely different method, in general confirm the conclusions reached by Dahms in a very satisfactory way.

The arrangement of apparatus was similar to that used in our first experiments on the decay of phosphorescence.¹ A spark was used for excitation and a shutter was so arranged that the screen was exposed to the infra-red rays and the phosphorescence light allowed to fall on the slit of the spectrophotometer at the same instant that the excitation was brought to a close by short circuiting the spark. A Nernst glower was used as a source of infra-red rays. This was mounted in the place of the slit of a large mirror spectrometer with quartz prism.² The Sidot blende screen was covered with black paper except for a narrow rectangular region having

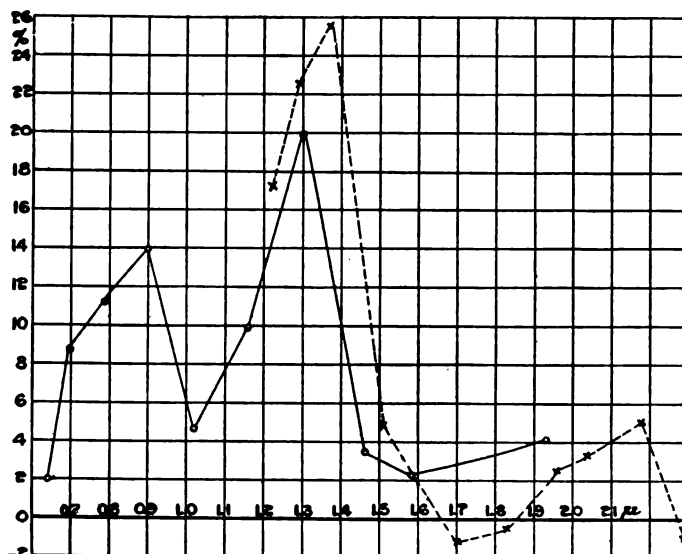


Fig. 68. Effect of infra-red rays of different wave-length. Ordinates represent the percentage diminution in the time of decay under the influence of infra-red.

about the same width as the Nernst glower. The adjustment of the spectrometer having been determined by observations in the visible spectrum, wave-lengths in the infra-red were computed from the angle of deviation. The effect of different rays from the Nernst glower was measured by the difference between the times required for the phosphorescence to fall from its initial intensity to a definite

¹ PHYSICAL REVIEW, Vol. 21, p. 247, 1905.

² Tests (by direct eye observation) with a rock salt prism showed that no effect was observable for wave-lengths longer than those transmitted by quartz.

final intensity with and without exposure to the rays to be tested. Each point on the curves shown in Fig. 68 is determined from the average of ten observations with infra-red and ten without, the observations being made alternately. The difference between the two, expressed as a fraction of the normal time of decay, has been plotted for the different wave-lengths used, which ranged from $0.6\ \mu$ to $2.3\ \mu$. The observations refer to the region of maximum intensity in the phosphorescence spectrum ($0.512\ \mu$).

Referring to Curve I., Fig. 68, it will be seen that the effect of the longer waves is observable to some extent in the visible region. A maximum is reached at about $0.9\ \mu$, followed by a minimum at about $1.0\ \mu$ and another maximum at $1.3\ \mu$. From $1.2\ \mu$ on the observations were repeated under slightly different conditions the following day. (Curve II.) In this case the chief maximum appears to lie at $1.37\ \mu$. The results are probably in all cases uncertain to the extent of 2 or 3 per cent., and errors are especially likely to be serious in regions where the effect is small. For this reason we cannot feel certain of the third maximum at $2.18\ \mu$, although the probability is that it really exists. As far as any important effect is concerned, however, our results confirm the conclusion of Dahms that the action does not extend beyond $1.5\ \mu$.

It can scarcely be doubted that absorption of the active rays is necessary before they can produce any effect upon phosphorescence. It seems probable, therefore, that Sidot blende possesses broad absorption bands with maxima not far from $0.9\ \mu$ and $1.37\ \mu$. Experiments with other phosphorescent substances having ZnS as their base will be necessary to determine whether the absorption that determines this effect on phosphorescence is characteristic of the solvent ZnS or of the dissolved metal causing luminescence. It is interesting to note, however, that in the absorption spectrum of sphalerite (ZnS) Coblenz has found evidence of bands at about $0.9\ \mu$ and $1.4\ \mu$. While Coblenz's work does not indicate great absorption at these points it must be remembered that they fall in the most intense region of the spectrum of a Nernst glower, so that the total amount of energy absorbed might be very considerable.

SOME ELECTRICAL PROPERTIES OF SILICON.

BY FRANCES G. WICK.

I. THERMO-ELECTRIC BEHAVIOR OF METALLIC SILICON.

THE physical properties of metallic silicon, in so far as they have been investigated, show this substance to be of peculiar interest. The position of the element in the periodic system between the metals and non-metals may explain some of the deviations of its properties from those of the stronger metals. It resembles carbon, which stands next above it in the same group, in that it is a poor conductor of electricity and has a negative temperature coefficient of resistance.

The work here given upon the thermal electromotive force of silicon is the first of a series of observations upon the properties of this element which have been undertaken by the writer at the suggestion of Professors Nichols and Merritt. The silicon used is the most recent product of The Carborundum Company. It was cast in rods about 30 cm. long and 3 mm. in diameter by H. E. Heath,¹ of The General Electric Company, of whose kindness the author wishes to express her appreciation. The Carborundum Company state that their commercial product is at least 95 per cent. pure, the chief impurities being iron and aluminum.²

The extreme hardness and brittleness of silicon made the manipulation of it very difficult, the greatest problem encountered being that of making good electrical contact. An attempt was made to solder terminals to it, but this was impossible. The best connections were made by copper-plating the silicon. Even this method was not entirely satisfactory, since the copper plate pulls off easily.

¹ Mr. Heath, recognizing the large thermal effect of silicon in combination with different metals, has patented a thermo-couple, one member of which is to be silicon. Patent No. 824,015. June 19, 1906.

² Tone, Trans. Am. Electro. Chem. Soc., Vol. VII., 1905.

The method of determining the E.M.F. generated by a thermo-electric couple made of copper and silicon was as follows: The ends of a silicon rod were copper plated. Upon each end of this rod were placed two wires, one of copper and one of constantan. The electro-plating process was then continued until these wires were firmly fastened to the silicon rod by a bridge of copper. Pipe stems were used for insulation. Copper wires were soldered to the ends of these wires as shown in Fig. 1, making in all three sets of thermo-junctions, one of copper-silicon, and firmly plated to each end of the silicon rod, one of copper-constantan. The copper-

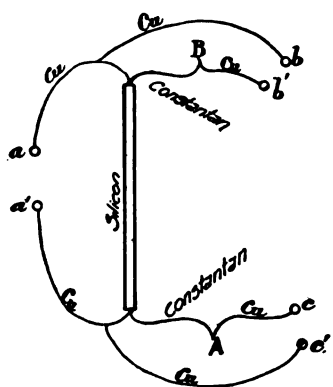


Fig. 1.

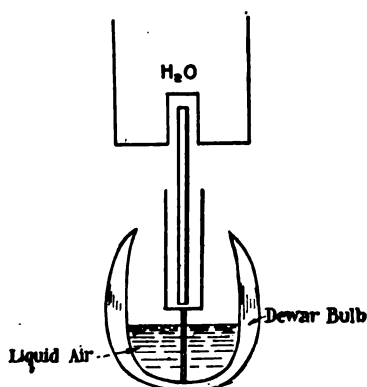


Fig. 2.

constantan couples were used for the determination of the temperature of the ends of the rod, the junctions not attached to the rod, *A* and *B* (Fig. 1), being kept at 0° .

The terminals of these thermo-elements *aa'*, *bb'*, *cc'* were dipped into mercury cups separated only by a thin layer of mica to avoid differences of temperature. Connections were thus easily made with potentiometer leads.

Measurements of thermal E.M.F. were made at temperatures ranging from about 350° to -190° C., one end of the rod being kept as near 0° as possible. Since the silicon rod is a good conductor of heat it was difficult to maintain the ends at a great temperature difference. For high temperatures the upper end of the rod was placed in a heating coil made of iron wire wrapped around a porcelain tube covered with asbestos. The lower end of the rod was

placed in a metal tube and this in a Dewar bulb containing a freezing mixture. For low temperature ranges the lower end of the rod was placed in a metal tube from which heavy copper wires projected into liquid air in a Dewar bulb, as shown in Fig. 2. By raising and lowering this tube temperatures varying from 0° to liquid air temperatures could be maintained. The upper end of the rod was kept at approximately 0° by means of a heating coil or by projecting upward into a tube surrounded by water of the required temperature.

It was often impossible to get steady conditions with one end of the rod exactly at 0° when the temperature of the other end was extremely high or low, hence a number of tests were carefully made covering the range of temperature through which the end of the rod varied from 0° . A curve was drawn showing the relation between the E.M.F. of the copper-silicon junction and a copper-constantan junction, one end of each being kept at 0° . By means of this curve the E.M.F. obtained was corrected to give that which would be obtained with one end of the rod at 0° .

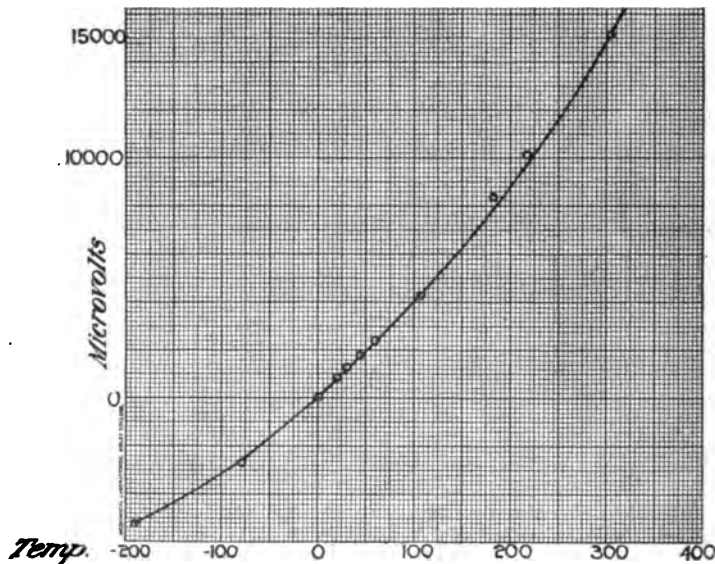


Fig. 3. Calibration curve of a copper constantan thermo-couple, one junction being kept at 0° .

The copper-constantan thermo-junctions on the ends of the rod were all made from the same spools of copper and constantan wire. A junction from these same spools had been made by Professor J. S. Shearer and calibrated from liquid air temperatures to the temperature of boiling benzophenone, the intermediate points being CO₂ and ether, water at temperatures from 0° to 100°, aniline and naphthalene. A similar junction made and calibrated through the same temperature range from -190° to +100° showed such agreement that the two calibration curves were identical.

TABLE I.

Rod No. 1. Length = 24.1 cm. Average Diameter = 3.24 mm. E.M.F. in Microvolts.

Copper-Constantan.		CuSi between (1) and (2).	CuSi between 0 and (2). From Calibration Curve.	CuSi between 0 and (1).	Temperature.
(1) Hot End.	(2) Cold End.				
541	100	-4,421	-950	-5,371	13.5°
842.5	247	-6,119	-2,367	-8,486	22.5
865	240	-6,187	-2,300	-8,487	22.5
840.5	254	-6,095.5	-2,450	-8,545.5	22.8
1,605.5	180	-14,135.5	-1,720	-15,855.5	40.5
1,611	174	-14,170	-1,670	-15,840	40.6
2,282.5	277	-19,531	-2,600	-22,131	56.4
2,283.5	275	-19,583.5	-2,550	-22,133.5	56.6
2,446	307	-20,874.5	-3,000	-23,874.5	59.8
2,456	311	-20,931	-3,050	-23,981	60.4
2,460	308	-20,949.5	-3,000	-23,949.5	60.5
2,466	317	-20,960	-3,100	-24,060	60.8
2,889	260	-25,217.5	-2,500	-27,717.5	70.3
5,713	528	-47,061	-5,170	-52,231	129.8
10,374.5	727	-80,105.5	-7,200	-87,305.5	215
12,020	738	-90,890	-7,320	-98,210	252
12,113.5	670	-92,381	-6,620	-99,001	255
16,666.5	693	-118,732.5	-6,850	-125,582.5	339
16,207	681	-119,145	-6,750	-125,895	340
16,846.5	648	-120,351	-6,400	-126,751	342
			CuSi between 0 and (1).	Computed CuSi between 0 and (2).	
617.5	-1,437	+19,218.5	-6,100	13,118.5	-36°
483.57	-2,408.55	+27,419.3	-4,740	22,679.3	-69
604.5	-2,590.25	+30,005.5	-6,350	23,655.5	-72
519.3	-3,694.8	+41,812.6	-4,980	36,832.6	-110.5
161.25	-4,814.5	+51,324.3	-1,500	49,824.3	-159
63.3	-5,340	+58,819.7	-570	58,249.7	-187

This calibration curve is given in Fig. 3. The high temperature points are those taken from the observations of Professor Shearer, the low temperature points being those taken by the author. After the tests on thermal E.M.F. of silicon were completed the silicon rod with its two attached copper-constantan junctions together with the previously calibrated copper-constantan junction was completely immersed in liquid air. Comparison of these three junctions showed no variation among them.

RESULTS.

The thermal E.M.F. between Cu and Si was thus obtained for three different rods. Tables I., II. and III. give the results. Table IV. gives the data used in drawing one of the calibration curves referred to above, from which the thermal E.M.F. which will be generated with one end of the rod at the given temperature and the other at 0° was computed. These curves are not reproduced here.

TABLE II.

Rod No. 3. Length = 21.2 cm. Average Diameter = 3.168 mm. E. M. F. in Microvolts.

Copper-Constantan.		CuSi between (1) and (2).	CuSi between o and (2).	Computed CuSi between o and (1).	Temperature.
(1) Hot End.	(2) Cold End.				
140	0	-2,055	0	-2,055	4°
687.5	0	-7,721	0	-7,721	20.4
3,290	199	-31,005	-2,400	-33,405	79.2
4,753	318	-42,307	-3,550	-45,857	111
4,956	336	-43,865	-3,750	-47,615	114
4,965	331	-43,926	-3,670	-47,596	116
4,970	333	-43,910.5	-3,700	-47,610.5	116
7,988.5	557	-65,848	-6,220	-72,068	176
11,895	736	-91,835	-8,250	-100,085.5	250
14,247.5	877	-105,422.5	-9,780	-115,202.5	289
			CuSi between o and (1).	Computed CuSi between o and (2).	
439.7	-2,148.3	25,733	-4,700	21,033	-58°
262.36	-2,681.8	34,470	-2,920	31,550	-78.5
153.5	-3,732	41,076	-1,700	39,376	-113.5
1,543	-5,181	78,589	-15,000	63,589	-178.5
1,541	-5,181	78,537.5	-15,000	63,537.5	-178.5
300.4	-5,202	67,411	-2,950	64,461	-182.5

TABLE III.

Rod No. 4. Length = 30 cm. Average Diameter = 3.34 mm. E.M.F. in Microvolts.

Copper-Constantan.		CuSi between (1) and (2).	CuSi between o and (2).	Computed Cu Si between o and (1).	Temperature.
(1) Hot End.	(2) Cold End.				
104	0	-1,106	0	-1,106	3.3
560.5	0	-5,675.5	0	-5,675.5	15
768.5	0	-7,870	0	-7,870	18.5
754	0	-7,568	0	-7,568	19.3
1,395	0	-14,358.5	0	-14,358.5	35.5
1,632.5	60	-16,106.5	-600	-16,706.5	41
3,277.5	136	-31,635	-1,400	-33,035	79
4,403.5	0	-43,182	0	-43,182	103
8,780.5	60	-78,420	-600	-79,020	190
			CuSi between o and (1).	Computed CuSi between o and (2).	
205	-2,681	31,671	-2,100	29,571	-78.4
0	-5,204	60,442.5	0	60,442.5	-179

TABLE IV.

Calibration of Copper-Silicon Junction Against Copper-Constantan—one end of each being kept at 0°. E.M.F. in Microvolts.

Copper-Constantan.	Copper-Silicon.
560	-5,532.5
210	-1,996.5
190	-1,870
830	-7,950
81	-720

The direction of the current was found to be from Si to Cu through the hot junction. Silicon is therefore thermo-electrically negative with respect to Cu. Since Pb is also negative with respect to Cu the E.M.F. which would be generated between Pb and Si must be the difference between that generated by Cu-Si and Cu-Pb junctions at the given temperature.

This difference was computed by a table given by Dewar and Fleming.¹ The resulting curves for rods no. 1 and no. 2 are given in Fig. 4. The bismuth line from Dewar and Fleming's table has been put in for comparison. The original curve for thermal E.M.F. between Cu and Si at low temperatures is given in Fig. 5.

¹ Dewar & Fleming, Phil. Mag., Vol. 40, p. 95, 1895.

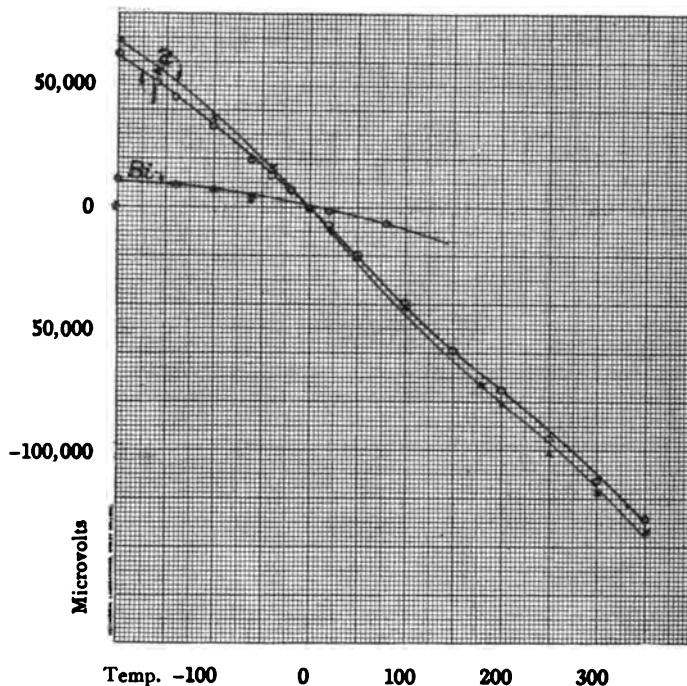


Fig. 4. Thermal E.M.F.

(1) Lead-silicon junction. Rod No. 1.

(2) Lead-silicon junction. Rod No. 2.

(B) Lead-bismuth junction.

Curves 1 and 2 were computed from Tables I. and II. and from copper-lead curve given by Dewar and Fleming.

It will be noticed that the thermal E.M.F. generated by a lead-silicon junction is very large. Another peculiarity about it is that the curve is not parabolic, being at least of the third degree. This double curvature may possibly be due to a large Thomson effect.

From curves drawn from the data given in Tables I. and II. the thermo-electric power of a silicon-copper junction was computed. This was done by finding the slope of these curves at intervals of 20° . The thermo-electric power line so found, given in Fig. 6, is not straight but has a maximum ordinate (negative) between 0° and 100° which diminishes as the temperature is raised or lowered.

The extremely large value of this thermal E.M.F. becomes evident by comparison with that produced by other metals in com-

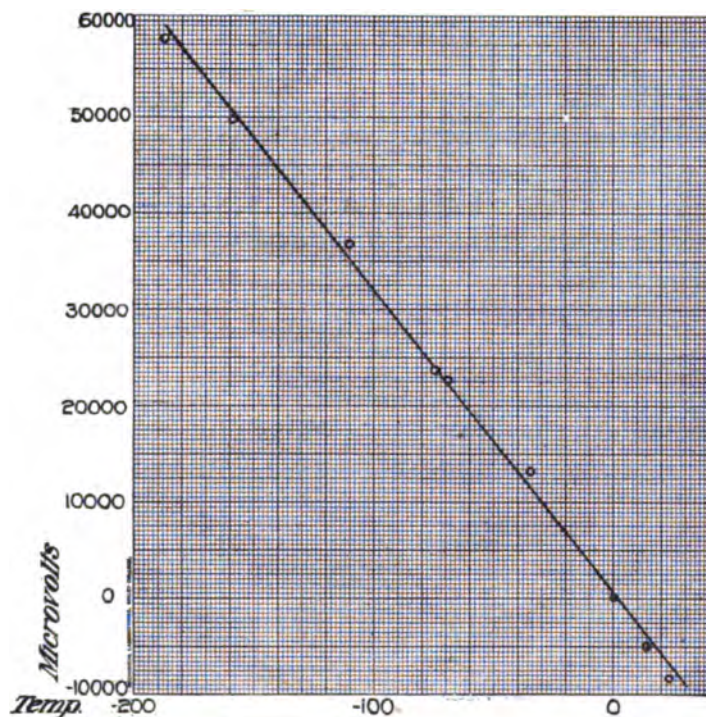


Fig. 5. Thermal E.M.F. between copper and silicon at low temperatures, one junction being kept at 0°.

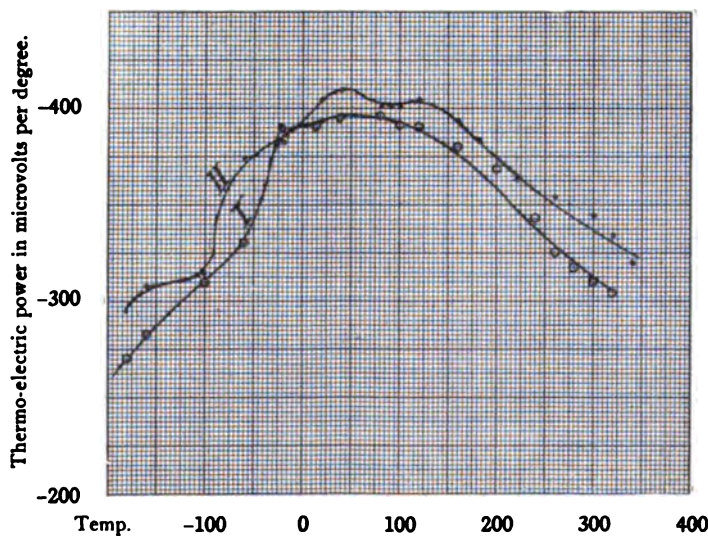


Fig. 6. Thermo-electric power of copper-silicon junctions in microvolts per degree centigrade.

Curve I. computed from measurements upon Rod No. 1.

Curve II. computed from measurements upon Rod No. 2.

bination with lead measured in microvolts per degree centigrade at a mean temperature of 20°C . At this temperature a lead-silicon junction gives a thermo-electric power of about -400 . The value for bismuth is -89 , for antimony $+26$. Tellurium and selenium are comparable with silicon but of opposite sign, being $+502$ and $+807$ respectively.

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CONDENSATION NUCLEI OBTAINED FROM THE EVAPORATION OF FOG PARTICLES.¹

BY C. BARUS.

1. *Standardization with Ions*.—A curious behavior appeared in an attempt to standardize the coronas of cloudy condensation by aid of the ions due to gamma rays penetrating the fog chamber. These were obtained from a sample of radium of strength 10,000 $\times$ and weighing 100 mg., sealed in an aluminum tube. The coronas were produced by successive exhaustions of the same value and the fogs were dissipated by compression, filtered air being introduced as soon as possible. The data obtained in the experiments showed an enormous initial loss. To obtain large coronas, the exhaustion to catch the ions was necessarily higher (drop of pressure $\delta p = 22.6$) than to catch the water nuclei resulting from the evaporation of fog particles ($\delta p = 17.1$); but this was allowed for.

The attempt to find the subsidence constant, S , fails; as for instance, if $s/30$ is the angular diameter of the coronas,

$s = 4.7$	3.3	2.0	1.0	4.4	3.0	1.8
$S = 12.2$	7.9	3.4		11.5	6.6	

showing a well marked progression of data. Similarly the attempt to find the initial nucleation n_0 fails, as a progression is here equally manifest. In other words, with the evaporation of the first fog (precipitated on ions) more than one half the nuclei are lost, whereas in subsequent evaporations, the behavior of the remaining nuclei is more like phosphorus nuclei, without evaporation losses.

That the discrepancy is in large measure due to the losses in the first evaporation will be seen if the second residue

$$(n \times 10^{-3} = 50.6)$$

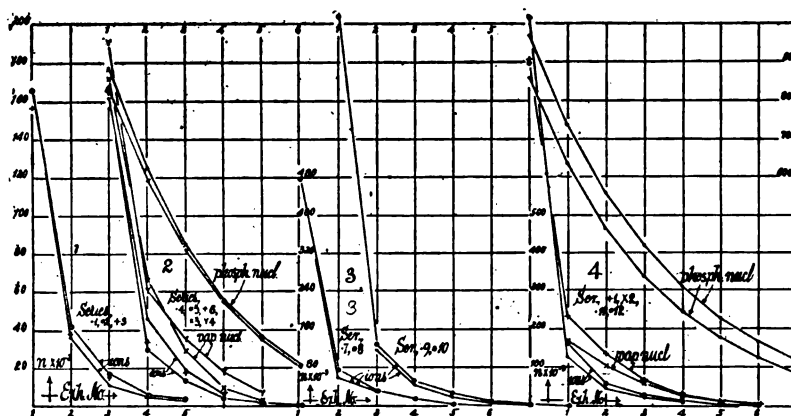
be taken as the initial number. The results are in thousands per cub. cm.

¹ Condensed from a report (now in preparation) to the Carnegie Institution of Washington.

	Nuclei Present.	Should be Present.	Nuclei Present.	Should be Present.
Ions.	$n = 76.9$	$n = 76.9$	$n = 76.9$	$n = 76.9$
After 1 evaporation.	22.3	50.6	18.3	50.6
" 2 evaporations.	7.7	8.0	5.8	6.2
" 3 "	1.7	.9	1.2	.4
" 4 "	.2	.1	.0	.0

2. *Systematic Data.*— Thus it appears that the water nuclei obtained by evaporating fog particles precipitated on ions vanish more rapidly, at least in the beginning, than may be accounted for as the combined result of the exhaustion applied and the subsidence. New results were therefore investigated by aid of the diffraction method¹ of two sources.

These are given in Figs. 1, 2, 3 and 4, where the ordinates show the number of nuclei caught in the successive identical exhaustions, and the abscissas the distributive number of the exhaustion



Figs. 1-4.

applied. Each exhaustion is followed by an evaporation of fog particles, whereby the residual water nuclei are produced for the next exhaustion in order.

In the first, second, and third series of experiments the exhaustion was somewhat above the condensation limit of air, so that the coronas do not vanish (Fig. 1). But as the vapor nuclei are rela-

¹ See Am. Journal of Science, XXIV., pp. 277-281, 1907.

tively few as compared with the ions, the initial fall of nucleation is well brought out. The exhaustion is here identical for ions and for water nuclei.

In series 4, 5, 6, the exhaustion for water nuclei is below the fog limit of air and the coronas vanish on successive exhaustion. It is necessary, therefore, to make the exhaustion for ions (only) above the condensation limit of air as otherwise too few would be caught. The observed march of data is however similar to the preceding experiments, as is shown in Fig. 2.

These results were now varied by bringing to bear stronger radiation obtained from an X-ray bulb placed at successively decreasing distances D from the fog chamber. In series 7 and 8, $D = 40$; in series 9 and 10, $D = 20$ cm.; and in series 11 and 12, $D = 12$ cm. (about) from the axis of the fog chamber. The large initial radiations drop off rapidly in the same way as in the preceding case. All the series are consistent, except the eleventh, in which the initial drop is too large compared with the others. It was customary to keep the exhaust cock open for five seconds, after which the filter cock was opened to dispel the fog, one minute being allowed between the exhaustions. The results are shown in detail in the figures together with similar data for the vapor nuclei of dust-free air and for phosphorus nuclei.

3. *Data for Vapor Nuclei.* — The figures contain similar data for the vapor nuclei of wet dust-free air. In series 1 and 2 large coronas or high nucleations are met with at the start, and they are compared in Fig. 4 with a corresponding case for ions. In series 3 and 4 lower initial nucleations are contained and these data are compared in Fig. 2 with the corresponding cases of ions and phosphorus nuclei. Corrections for subsidence should have been added to the graphs for ions and for vapor nuclei, but these are not large enough to modify them materially, so far as the figures go.

4. *Remarks on the Results.* — The graphs in Figs. 2 and 4 show unmistakably that the water nuclei obtained from the evaporation of fog particles precipitated on ions, vanish in the successive exhaustion faster than in the corresponding case with the vapor nuclei of dust-free air; while the water nuclei from fog particles precipitated on vapor nuclei vanish much faster than is the case for the corre-

sponding solutional nuclei obtained with phosphorus emanation. It is thus necessary to examine in detail the three more obvious causes for the decrease in the number of nuclei, which are as follows: (1) the exhaustions applied alike in all cases; (2) the subsidence of fog particles during the short time of their suspension, *i. e.*, between the exhaustion and the evaporation by influx of air; (3) the occurrence of electrical charge in the case of ionized nuclei whereby the charged water nuclei may be brought to coalescence.

Probably the best method of reaching a numerical result will consist in eliminating the effect of exhaustion and subsidence as was done for phosphorus nuclei, thus leaving the new losses of nuclei alone outstanding. If n_s' is the nucleation of the s th exhaustion,

$$n_s' = n_1 \gamma^{s-1} \Pi (1 - S/s_{s-1}^2),$$

where γ is the exhaustion ratio and the product $\Pi (1 - S/s_{s-1}^2)$, the correction for subsidence, the data obtained are such as apply for solutional nuclei produced by phosphorus; but they are throughout enormously in excess of the values n_s observed for vapor nuclei and for ions. Supposing that there is a second cause of dissipation with each exhaustion the equation may be written (abbreviating the products Π)

$$n_s' = n_1 \gamma^{s-1} x^{s-1} \Pi$$

merely to get a numerical statement of the case. The values of x so found show a gradual increase, as the numbers of exhaustions increase or the nucleations decrease and the sizes of fog particles increase, so that the greatest dissipation of nuclei occurs during the first exhaustion.

If these values of x are summarized and constructed in terms of n , they also show that x is considerably in excess for vapor nuclei as compared with ions.

The best method of interpreting the above results is in terms of an equation of the form (if n_1 be the initial nucleation)

$$n_s = n_1 \gamma^{s-1} x x' x'' \dots \Pi,$$

where n_s is the nucleation of the s th exhaustion, γ the exhaustion ratio, the product Π the subsidence correction and $x, x', x'',$ etc., the successive coefficients showing the relative survival, x , or the

corresponding loss, $(1-x)$, of nuclei, accompanying each evaporation of the fog particles. This equation asserts that the loss is different in the successive evaporations, which is actually the case in question.

So treated the results indicate the degree to which the first evaporation is preponderating and prove it to be more destructive, as the original number of ions is greater. Thus when $n = 160,000$, $(1-x)$ or 60 to 70 per cent. are lost during the first and only about $(1-x')$ or 20 per cent. during the second or subsequent evaporations. If $n = 900,000$ to 1,100,000 (where the fog particles are very much smaller), the first destroys about 80 per cent., the second 40 per cent., the third 30 per cent. of the number which happen to be present just before the respective evaporation. Hence for large values of n the loss due to evaporation is appreciable throughout many repetitions.

The results, for fog articles precipitated upon the vapor nuclei of dust-free air are similar, but in no case does the coefficient of survival x increase after the first exhaustion, as was the case with ions. Contrasting the case of ions with the case for vapor nuclei, specifically, the coefficient of survival x is always decidedly smaller for ions in the first exhaustion than for vapor nuclei. The charged nuclei are therefore destroyed in greater number than uncharged nuclei by the evaporation of fog particles precipitated on them. When the number of nuclei is large (10^6), this is also true in subsequent evaporations, though the contrast is less marked.

Another question which comes up for settlement is this: Whether the fog particles which are represented by nuclei after evaporation are above a certain critical size, and those particles which vanish are below it. This is hardly probable because all the fog particles contribute to the same corona and because it implies an enormous inequality in the fog particles of the first exhaustion, seeing that 45 per cent. to 85 per cent. vanish in the different cases cited. These results for the diameters d of fog particles and the corresponding coefficients of survival x , x' , etc., are constructed graphically in Fig. 5, *a*, *b*, for ions and in Fig. 5, *c*, *d*, for water nuclei.

Fig. 5, *a*, containing series 4 to 8 for small ionized nucleations (below $n = 500,000$), suggests that x may change abruptly when

$d = .0006$ cm.; while Fig. 5 *b*, for large ionized nucleations, 10^6 , has the same appearance at $d = .0005$ cm. However, this is nothing more than the transition from the first to the second evaporation, the former being so much more efficient.

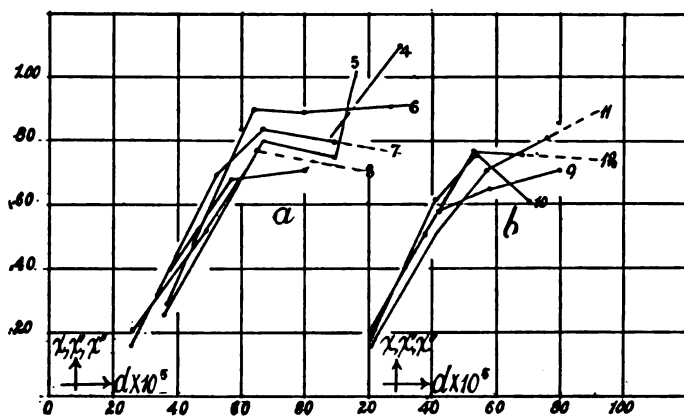


Fig. 5.

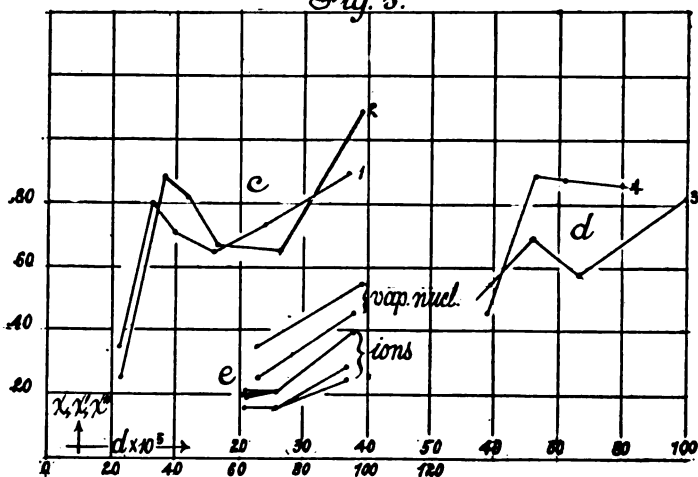


Fig. 5, *c* and *d*, for large and small nucleations of vapor nuclei has the same character. In *c* for instance there is an abrupt change below 40,000 nuclei. But the case is again one instancing the paramount importance of the first evaporation.

There is, however, no doubt of an outstanding effect due to the number or the size of the nuclei. The coefficient of survival x de-

creases as the number of nuclei increases, or better as their size diminishes. Thus if the comparison be restricted to the first evaporation, Fig. 5 *e*,

Ions :	$10^5 d = 38$		37	37	26	26	21	22	21	21 cm.
	$10^5 x = 40$		25	29	16	21	19	21	16	20
Vapor nuclei :	$10^5 d = 39$		38		23	23 cm.				
	$10^5 x = 55$		46		25	25				

from which the increase of x with the size of the particles is put beyond question and the larger coefficient of survival for vapor nuclei as compared with ions is again apparent. Whether the peculiar features of the curve, Fig. 5 *c*, which reappears in each case, have a definite meaning must be left to conjecture ; but in most of the curves, *a*, *b*, *c*, *d*, the occurrence of maximum x is in evidence.

6. *Loss of Nuclei Actually Due to Evaporation.* — It is finally to be shown that the peculiar loss of water nuclei resulting after evaporation of fog particles precipitated upon ions is due to this evaporation (or its equivalent) and not to the dissipation of the water nuclei in the lapse of time. It might be supposed for instance that water nuclei obtained from the fog condensed on the ions are smaller and therefore diffuse more rapidly than water nuclei obtained by other methods. If so, then if the time between the successive exhaustions is doubled, trebled, etc., the loss should be correspondingly increased. Data investigated on the above plan but containing the time interval, t , in minutes between the exhaustions, shows that the time effect is secondary. The interval t was varied from 1 to 6 minutes.

If the results are constructed in a figure like the above, the abscissa being the time in minutes, the ordinates showing the nucleation, the curves indicate a steady progression towards the right as the time interval increases, showing that the time losses although not necessarily absent are not of relevant importance. In fact the group of observations for one minute and six minute intervals, constructed in terms of the number of exhaustions (ignoring lapse of time), are virtually coincident. Again the curve for two minute intervals actually shows less loss (due to favorable exhaustion conditions) than the curve for one minute interval.

In one series of experiments, radium was left in place except during the exhaustion (for ions are efficient in presence of water nuclei). It was found that the water nuclei stored in this ionized field do not decay more rapidly than in ordinary dust free wet air.

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THE DIURNAL VARIATION OF THE SPONTANEOUS IONIZATION IN AIR IN CLOSED METALLIC VESSELS.

BY T. FREDERICK MCKEON.

INTRODUCTION.

AIR and other gases within closed metallic vessels are found to possess a slight conductivity even when not acted upon by an artificial ionizing agent. For a time it was thought that the presence of these free ions in the gas was due to an intrinsic property of the gas by which it was capable of ionizing itself. Recent investigations, however, have shown that some at least of these free ions must be attributed to the action of external agents. McLennan and Burton¹ measured the natural conductivity of the air in a large closed metal cylinder by means of a sensitive electrometer, and found that when the cylinder was completely surrounded with water the saturation current, or leak, through the vessel was greatly reduced. Rutherford and Cooke² observed that the rate of discharge of a sealed glass electroscope was diminished by placing a lead screen around the electroscope. Cooke³ continued the investigation of the decrease of the rate of discharge in the electroscope, when surrounded by metal screens, and found that a thickness of 5 cm. of lead around the electroscope decreased the rate of discharge about 30 per cent., while further increase in thickness of the screen had no effect. An iron screen also diminished the rate of discharge to about the same extent as the lead.

A. Wood⁴ has found that the diminution of the ionization by a given screen depended upon the material of the vessel. The ionization in a lead vessel surrounded by a lead screen was reduced 10

¹ *Phys. Rev.*, V. 16, p. 185, 1903, and *Phil. Mag.*, V. 5, p. 419, 1903.

² *Amer. Phys. Soc.*, Dec., 1902.

³ *Phil. Mag.*, Vol. 6, p. 403, 1903.

⁴ *Phil. Mag.*, Vol. 9, p. 550, 1905.

per cent., while in an iron vessel it was reduced 24 per cent. Wood concludes from his experiments that the ionization observed in a closed vessel has a threefold origin. A part of it is due to an external penetrating radiation, part to a secondary radiation set up by it, while the remainder is due to an intrinsic radiation from the walls, altogether independent of the external radiation.

Patterson¹ examined the variation of the ionization of air with pressure in a large iron vessel of diameter 30 cm. and length 20 cm. The current between a central electrode and the cylinder was measured by means of a sensitive electrometer. He found that the saturation current was practically independent of the pressure for pressures greater than 300 mm. of mercury. Below a pressure of 80 mm. the current varied directly as the pressure. For air at atmospheric pressure the current was independent of the temperature up to 450° centigrade. With further increase of the temperature the current began to increase. The current was more rapid when the central electrode was charged negatively than when it was charged positively. This difference was ascribed to the production of positive ions at the surface of the iron vessel.

Strutt,² by means of an electroscope, observed that the ionization produced in a closed vessel varied with the material of the vessel. He found considerable differences, however, between different samples of the same material, and was inclined to conclude that the intrinsic radiation from the walls of the vessel was due to traces of radioactive impurities. A. Wood, working in the Cavendish Laboratory, repeated the experiments of Strutt, but failed to observe any differences in the ionization produced by different samples of the same material. The order of activity which he observed for the different materials was the same as that given by Strutt, with one exception. Similar experiments by McLennan and Burton, and Campbell confirmed the order obtained by these two observers. These experiments of McLennan and Burton, Wood, Strutt, and the others show that part of the spontaneous ionization in a closed vessel containing gas is due to the influence of the walls. H. L. Cooke has observed also that the ionization of the air in a brass electroscope could be

¹ *Phil. Mag.*, Vol. 5, p. 680, 1903.

² *Phil. Mag.*, Vol. 5, p. 680, 1903.

reduced to about a third of its usual value if the interior surface of the brass was carefully cleaned. By removing the surface of the brass he was able to reduce the ionization of the inclosed air from from 30 to 10 ions per c.c. per second. This is an important observation, and, as Rutherford has indicated, shows that a large proportion of the radio-activity observed in ordinary matter is due to a deposit of radio-active matter on the surface. It is well known that bodies which have been exposed in the presence of an emanation retain a residual activity, which takes some time to die out. The experiments of Bumstead¹ prove beyond a doubt that radium and thorium emanations exist in the atmosphere, and we may reasonably suppose that the exposed surface of matter, in consequence, will become coated with an invisible film of radio-active matter deposited from the atmosphere.

The experiments described in this paper were primarily undertaken with a view to ascertaining the modifications that should be introduced in the results of experiments such as were carried out by McLennan and Burton, if material was made use of which had been exposed to the atmosphere for a long time. To this end material was selected from a supply purchased some ten years previous to the carrying out of the experiments. This supply had been stored in the machine shop connected with the Department of Physics at the time of purchase, and the portion used had remained practically undisturbed up to the time of carrying out these experiments. The method followed was practically the same as that employed by McLennan and Burton, except that the cylinders used were considerably smaller than theirs. The results of the first few experiments showed surprising variations in the leak. These variations, which could not be accounted for by any of the known properties of the emanations of the radio-active bodies, were attributed to defects in experimental arrangements, and the method was abandoned in favor of a method, which will be described shortly, and which is in the main due to McLennan. However, the same obstacle to the accurate study of the radio-activity of the material employed was encountered. The leak again showed daily, and even hourly variations. A systematic study of these variations was now begun, and consid-

¹ Amer. Jour. of Science, Vol. 8, p. 1, 1904.

erable evidence had been obtained, which tended to show that the variations follow some law, when the writer received the recent article by Wood and Campbell,¹ and became aware that they had made the study of the variations, and had given a preliminary account of their results in a letter to *Nature*, as early as April, 1905. Since, however, the method of experimenting was different from that of Wood and Campbell, and the results obtained point to a different conclusion than that given in their recent account of their complete study of the phenomena, and, moreover, since all the data so far available upon which to base the law of the daily variation of the ionization in closed vessels had been obtained in only two places (Cambridge and St. Petersburg), it appeared that the problem justified a complete investigation. The work described in the following pages resolves itself into three parts: (1) an investigation of the leak between two cylinders of the same metal, (2) an investigation of the leak between cylinders of different metals, (3) and principally, a study of the daily variation of the leak between the cylinders.

APPARATUS AND CONNECTIONS.

In the experiments of McLennan and Burton, already referred to, the apparatus consisted of two cylinders, one placed within the other, and insulated from it. The outer cylinder was hermetically sealed and connected to earth. The inner was connected with one pair of quadrants of an electrometer. Rather large cylinders were used. The outer ones were 120 cm. in length, and 24 cm. in diameter, the inner cylinders were 110 cm. in length, and 19 cm. in diameter. In the experiments described in this paper much smaller cylinders were used; the outer ones being 60 cm. in length and 15 cm. in diameter, and the inner 55 cm. in length and 4 cm. in diameter. The arrangement of the apparatus, which differs from that of the authors named above in minor details only, is outlined in Fig. 1. *A* represents the outer cylinder, and *B* the inner cylinder between which the leak is to be measured. The cylinders are insulated from each other by blocks of paraffin and ebonite. A short brass rod, in metallic connection with *B*, passes through an ebonite plug fitted into *A*, and is protected by an earth-connected guard

¹ Phil. Mag., Feb., 1907.

ring. The brass rod projects a short distance within a tube also of brass; a hole in the top of the tube permits connection to be made between the brass rod and a fine copper wire stretched along the

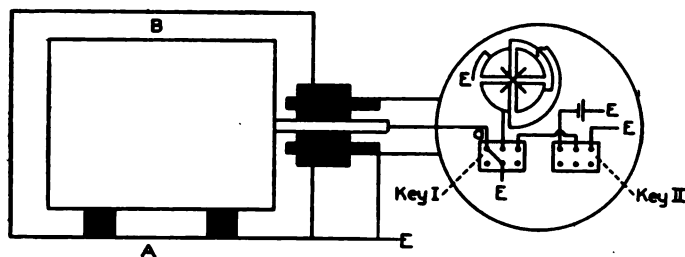


Fig. 1.

axis of the tube, and insulated from it by means of ebonite plugs. One end of this wire dipped into a mercury cup in a block of ebonite.

The electrometer used was of the Dolezalek type with amber insulation and adjustable quadrants. The needle was of silvered paper, and the suspension a quartz fiber dipped in a solution of calcium chloride to render it conducting. The needle was permanently connected with the negative pole of a Dolezalek-Nernst dry pile which kept its potential constant. The positive pole of the pile was connected to earth. The electrometer needle had a period of 60 seconds, and the damping was sufficient to make it dead beat. The zero position was fairly constant, the needle, except in one instance, not drifting through more than 2 cm. during the whole time of an experiment which was usually continued for more than four days. The sensibility did not vary appreciably during the same time.

The necessary connections were made with two simple trip keys which rested in mercury cups in a block of ebonite, and were worked mechanically, from a distance, by means of fine silk threads. A forward movement of key No. I., at the same time, broke the earth connection of the testing vessel, the earth connection of one pair of quadrants of the electrometer, and connected the vessel with the quadrants. When it was necessary to find the value of the scale readings in volts, a backward movement of key No. I. and a forward movement of key No. II. broke the earth connection of the

free quadrants, and connected them with the negative pole of a Carhart-Clark standard cell. The positive pole of the cell was earthed. The connections are given in outline in Fig. 1.

As very small potential differences had to be measured it was necessary to guard carefully against external electrostatic disturbances. The electrometer, the pile, which gave the charge to the needle, the keys for making connections, and the standard cell rested upon a wall shelf covered with tin-foil which was connected to earth. The electrometer, keys, etc., were covered with an earthed metallic screen made of wire, having twenty-five meshes to the square centimeter, covered with tin-foil. This screen proved most satisfactory, and protected completely against all external disturbances. The connecting wire between the testing vessel and the electrometer was inclosed in an earth-connected metallic tube.

METHOD OF WORKING.

After the outer cylinder had been adjusted upon two insulating blocks of ebonite, the inner cylinder and the insulating supports were placed in position within. A brass disk was inserted in the open end of the outer cylinder, and the joint thus made rendered air tight with paraffin wax. Connection was then made between the brass rod joined to the central cylinder and the wire, which dipped into the mercury cup *a*. The outer cylinder and the brass tube surrounding the connecting wire were next earthed. When the vessel was thoroughly sealed the free quadrants and the central cylinder were connected together, and their earth connections broken. The quadrants began at once to acquire a charge, which varied in intensity with the metals used. Because of the nature of the experiments, it was thought advisable to use a constant deflection method of measuring the current, and at the same time to avoid the complications which would arise from the use of resistance in parallel with the free quadrants. Under these circumstances the determination of the amount of charge to give the needle in order to obtain the maximum sensibility without causing the needle to deflect off the scale was a matter of several tests in almost every experiment. In case the current to be measured produced a deflection larger than could be measured on the scale, the sensibility

of the electrometer was reduced by decreasing the charge on the needle. The manner of determining this necessary charge was as follows: The central cylinder and free quadrants were connected together and insulated. The quadrants were then permitted to charge up until it was certain that the deflection would go beyond the limits of the scale, when the connection between the cylinder and quadrants was broken, and both were put to earth. The charge on the needle was then decreased, and the zero and sensibility redetermined. A number of tests of the constancy of these quantities was made after each change. It was found that if the needle was given a deflection a few times by connecting the quadrants to the standard cell, it settled down to a certain zero to which it always returned on further deflection in the same manner. Furthermore, it was found that all changes in the sensibility between observations taken within a few minutes of each other could be traced to imperfect conductivity of the quartz fiber, and could be entirely eliminated by redipping the fiber. When perfect constancy of zero and sensibility were attained, the cylinder and quadrants were once more connected together, and insulated. If the needle was again deflected beyond the limits of the scale the process was repeated, and this as often as was necessary, until the whole amount of deflection could be read. As ordinarily used the needle was kept at a difference of potential sufficient to give a deflection of 14 cm. on a scale at 120 cm. distance from the electrometer for a potential difference of one volt between the quadrants.

As a rule, an hour or more from the time the apparatus was sealed up and the quadrants first insulated, was spent in adjusting the charge on the needle so as to give the proper sensibility and finding the value of the scale readings in volts. Readings were begun immediately on insulating the quadrants, the spot of light from the mirror being read on a scale in the ordinary way. However, none of the readings taken before the final adjustment of the sensibility are given in this paper. For the first hour or two, from the beginning of the experiment, readings were taken every 3 or 7.5 minutes depending upon the rapidity with which the quadrants charged up. After that readings were taken at intervals of 12 or 15 minutes for 100 hours or more in each experiment.

It is evident that the method here outlined is open to some, though not serious, objections. First of all the method of rendering the needle conducting prevents the continuation of an experiment for any great length of time, and the necessity of regulating the sensibility of the electrometer makes it impossible to obtain the complete ionization curve from the time of sealing the apparatus.

RESULTS OF EXPERIMENTS.

In the experiments cylinders of lead, tin, aluminum and brass were used. Observations of the effect produced by combinations of these metals are set forth in the accompanying figures, where curves are drawn with the time expressed in hours of the day for abscissas and the deflection of the needle in arbitrary scale divisions for ordinates. It will be noticed that the variation of the ionization for all combinations of metals tried show three distinct characteristics. On connecting the central cylinder with the quadrants and insulating, the quadrants gradually acquire a charge which attains a maximum in a few hours, and then falls off, but never dies out altogether, or changes sign. This initial rise was observed by McLennan and Burton, but in their experiments the ionization did not fall off with time. When the experiments have been continued for 20 hours or more, the character of the phenomenon changes. At the end of this time the ionization has fallen to its lowest value, and the influence of two weak, but very definite sources of ionization, manifest themselves. The effect of the one is a progressive increase or decrease of the ionization, which is very evident when the experiment is continued for some days. Riding upon this progressive change in the ionization there is a change of periodic character, which has two maxima and two minima each 24 hours. Some evidence of the existence of this diurnal variation had been obtained already by different observers, but Wood and Campbell alone have pointed out that the daily period is twofold. A more complete understanding of what takes place will be gained by a detailed study of each curve.

ALUMINUM IN BRASS.

An inspection of the curves for aluminum within brass, Figs. 2 and 3, gives unmistakable evidence of these respective changes in

the ionization. The first curve, Fig. 2, shows the initial rise, which takes place on insulating the quadrants, and also the way the ionization falls off with time following this initial rise. A maximum is



Fig. 2.

reached in about 6 hours, and in 22 hours the leak has fallen to a minimum. The subsequent periodic variations which take place in the leak, are already manifest in the latter part of this curve, but are made much more evident in the second curve, Fig. 3, which is plotted on a different scale. A period of 36 hours elapsed between

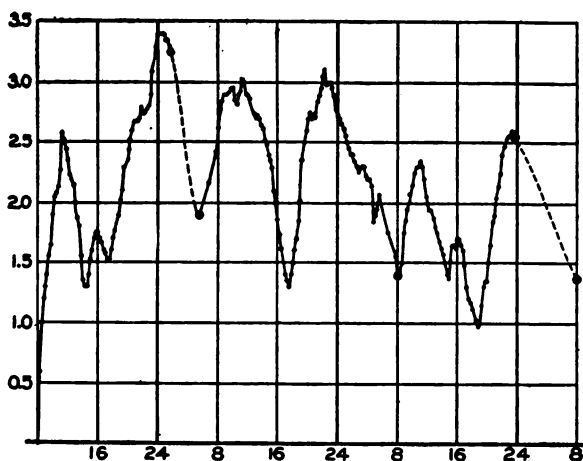


Fig. 3.

taking the observations plotted in the first curve and those plotted in the second, the quadrants in the meantime remaining insulated. This second curve shows a well-marked maximum for each day, at

Aluminum Cylinder within Brass Cylinder. Observations.

First Period. April 12, 1907. P. M.

Time. ¹	Scale Reading.	Amount of Deflection.	Time.	Scale Reading.	Amount of Deflection.
5.41	26.4	0.	1.48	8.52	17.88
5.44	25.25	1.15	2.	8.75	17.65
5.47	24.65	1.75	2.12	9.04	17.36
5.50	24.5	1.9	2.24	9.15	17.25
5.55	23.9	2.5	2.36	9.55	16.85
6.41	20.05	6.35	2.48	9.7	16.7
6.54	18.7	7.7	3.	9.8	16.6
7.	17.9	8.5	5.20	13.7	12.7
7.12	16.75	9.65	6.58	16.15	10.25
7.24	15.55	10.85	7.54	16.9	9.5
7.36	14.45	11.95	8.24	17.2	9.2
7.48	13.5	12.9	8.36	17.25	9.15
8.	12.6	13.8	8.48	17.43	9.06
8.12	11.78	14.62	9.	17.65	9.75
8.24	10.8	15.6	9.12	17.8	9.6
8.36	10.25	16.15	9.24	18.	8.4
8.48	9.55	16.85	9.36	18.18	8.22
9.	9.05	17.35	9.48	18.4	8.
9.12	8.4	18.	10.	18.51	7.89
9.24	7.96	18.44	10.12	18.65	7.75
9.36	7.64	18.76	10.24	18.88	7.52
9.48	7.28	19.12	10.36	18.95	7.45
10.	7.	19.4	10.48	19.15	7.25
10.12	6.95	19.45	11.	19.45	6.95
10.24	6.84	19.56	11.12	19.52	6.88
10.36	6.48	19.92	11.24	19.8	6.6
10.48	6.38	20.02	11.36	20.	6.4
11.	6.28	20.12	11.48	20.	6.4
11.12	6.25	20.15	12.	20.2	6.2
11.24	6.38	20.02	P. M.		
11.36	6.35	20.05	12.12	20.4	6.
11.48	6.3	20.1	12.24	20.6	5.8
12.	6.36	20.4	1.18	21.15	5.25
April 13. A. M.			1.36	21.3	5.1
12.12	6.42	19.98	1.48	21.4	5.
12.24	6.5	19.9	2.	21.55	4.85
12.36	6.7	19.7	2.12	21.7	4.7
12.48	7.3	19.1	2.24	21.8	4.6
1.	7.7	18.7	2.36	21.89	4.51
1.12	8.	18.4	2.48	22.	4.4
1.24	8.3	18.1	3.	22.17	4.23
1.36	8.5	17.9	3.12	22.35	4.05

¹As given by ordinary watch.

Aluminum Cylinder within Brass Cylinder. Observations.—Continued.

Time.	Scale Reading.	Amount of Deflection.	Time.	Scale Reading.	Amount of Deflection.
3.24	22.43	3.97	2.30	26.6	1.3
3.36	22.55	3.85	2.45	26.5	1.4
3.48	22.63	3.77	3.	26.38	1.52
4.10	22.4	4.	3.15	26.3	1.6
4.30	22.18	4.22	3.30	26.2	1.7
4.45	22.09	4.33	3.45	26.15	1.75
5.	22.05	4.35	4.	26.15	1.75
5.15	22.	4.4	4.15	26.21	1.69
5.35	22.06	4.34	4.30	26.24	1.66
6.30	22.	4.4	4.45	26.3	1.6
6.50	22.05	4.35	5.	26.33	1.57
7.	22.05	4.35	5.15	26.38	1.52
7.12	22.3	4.1	5.30	26.38	1.52
7.30	22.25	4.15	5.45	26.3	1.6
8.15	22.1	4.3	6.	26.2	1.7
Second period. April 15. A. M.			6.15	26.13	1.77
8.15	27.3	+ .6	6.45	26.	1.9
8.30	26.9	1.	7.	25.86	2.04
8.45	26.7	1.2	7.15	25.72	2.18
9.	26.6	1.3	7.30	25.6	2.3
9.15	26.5	1.4	7.45	25.55	2.35
9.30	26.35	1.55	8.	25.46	2.44
9.45	26.26	1.64	8.15	25.38	2.52
10.	26.	1.9	8.30	25.3	2.6
10.15	25.85	2.05	8.45	25.22	2.68
10.30	25.82	2.08	9.	25.22	2.68
10.45	25.73	2.13	9.15	25.22	2.68
11.	25.63	2.27	9.30	25.2	2.7
11.15	25.33	2.57	9.45	25.1	2.8
11.30	25.38	2.52	10.	25.16	2.74
11.45	25.46	2.44	10.15	25.15	2.75
12.	25.55	2.35	10.30	25.12	2.78
P. M.			10.45	25.1	2.8
12.15	25.67	2.23	11.	25.	2.9
12.30	25.7	2.2	11.15	24.8	3.1
12.45	25.75	2.15	11.30	24.7	3.2
1.	25.9	2.	11.45	24.6	3.3
1.15	26.02	1.88	12.	24.5	3.4
1.30	26.1	1.8	April 16. A. M.		
1.45	26.35	1.55	12.15	24.5	3.4
2.	26.55	1.35	12.30	24.5	3.4
2.15	26.5	1.3	12.45	24.5	3.4

Aluminum Cylinder within Brass Cylinder. Observations.—Continued.

April 16. A. M.

Time.	Scale Reading.	Amount of Deflection.	Time.	Scale Reading.	Amount of Deflection.
1.	24.55	3.35	5.	26.5	1.4
1.15	24.55	3.35	5.15	26.55	1.35
1.30	24.6	3.3	5.30	26.6	1.3
1.45	24.65	3.25	5.45	26.5	1.4
5.25	26.	1.9	6.	26.4	1.5
6.48	25.72	2.18	6.15	26.3	1.6
7.45	25.47	2.43	6.30	26.2	1.7
8.	25.28	2.62	6.45	26.05	1.85
8.15	25.13	2.77	7.	25.88	2.02
8.30	25.05	2.85	7.15	25.54	2.36
8.45	25.	2.9	7.30	25.4	2.5
9.	25.	2.9	7.45	25.3	2.6
9.15	25.	2.9	8.	25.2	2.7
9.30	24.98	2.92	8.15	25.15	2.75
9.45	24.95	2.95	8.30	25.2	2.7
10.	24.95	2.95	8.45	25.16	2.74
10.15	25.05	2.85	9.	25.18	2.72
10.30	25.08	2.82	9.15	25.05	2.85
10.45	25.	2.9	9.30	25.	2.9
11.	24.98	2.92	9.45	24.95	2.95
11.15	24.87	3.03	10.	24.84	3.06
11.30	24.9	3.	10.15	24.86	3.14
11.45	25.	2.9	10.30	24.91	2.99
12.	25.01	2.89	10.45	24.9	3.
12.15	25.03	2.87	11.	24.9	3.
12.45	25.17	2.73	11.15	24.95	2.95
P. M.			11.30	25.	2.9
1.	25.2	2.7	11.45	25.12	2.78
1.15	25.18	2.72	12.	25.16	2.74
1.30	25.2	2.7	April 17. A. M.		
1.45	25.25	2.65	12.15	25.2	2.7
2.	25.28	2.62	12.30	25.24	2.66
2.15	25.33	2.57	12.45	25.28	2.62
2.30	25.41	2.49	1.	25.34	2.56
2.45	25.5	2.4	1.15	25.4	2.5
3.	25.55	2.35	1.30	25.44	2.46
3.15	25.61	2.3	1.45	25.5	2.4
3.30	25.8	2.1	2.	25.5	2.4
3.45	25.9	2.	2.15	25.55	2.35
4.	26.05	1.85	2.30	25.6	2.3
4.15	26.16	1.74	2.45	25.64	2.26
4.30	26.28	1.62	3.	25.61	2.29

Aluminum Cylinder within Brass Cylinder. Observations.—Continued.

Time.	Scale Reading.	Amount of Deflection.	Time.	Scale Reading.	Amount of Deflection.
3.15	25.6	2.3	2.30	26.5	1.4
3.30	25.61	2.29	2.45	26.53	1.37
3.45	25.67	2.23	3.	26.38	1.52
4.	25.7	2.2	3.15	26.25	1.65
4.15	25.7	2.2	3.30	26.25	1.65
4.30	25.75	2.15	3.45	26.28	1.62
4.45	26.05	1.85	4.	26.2	1.7
5.	26.	1.9	4.15	26.2	1.7
5.15	25.95	1.95	4.30	26.25	1.65
5.30	25.83	2.07	4.45	26.3	1.6
6.53	26.15	1.75	5.	26.43	1.47
7.45	26.35	1.55	5.15	26.6	1.3
8.	26.5	1.4	5.30	26.7	1.2
8.15	26.48	1.42	5.45	26.73	1.17
8.30	26.4	1.5	5.55	26.78	1.12
8.45	26.15	1.75	6.25	26.85	1.02
9.	26.05	1.85	6.45	26.93	.97
9.15	25.95	1.95	7.	26.9	1.
9.30	25.82	2.08	7.15	26.75	1.15
9.45	25.88	2.02	7.30	26.6	1.3
10.	25.75	2.15	7.45	26.55	1.35
10.15	25.65	2.25	8.	26.55	1.35
10.30	25.6	2.3	8.15	26.4	1.5
10.45	25.6	2.3	8.30	26.25	1.65
11.	25.55	2.35	8.45	26.05	1.85
11.15	25.6	2.3	9.	26.	1.9
11.30	25.7	2.2	9.15	25.84	2.06
11.45	25.84	2.06	9.30	25.75	2.15
12.	25.9	2.	9.45	25.65	2.25
P. M.			10.	25.5	2.4
12.15	25.96	1.94	10.15	25.43	2.47
12.30	25.96	1.94	10.30	25.37	2.53
12.45	26.03	1.87	10.45	25.35	2.55
1.	26.1	1.8	11.	25.34	2.56
1.15	26.15	1.75	11.15	25.3	2.6
1.30	26.22	1.68	11.30	25.3	2.6
1.45	26.28	1.62	11.35	25.35	2.55
2.	26.33	1.57	April 18. A. M.		
2.15	26.4	1.5	8.	26.53	1.37

a time varying from 22.5 hours (10.30 P. M.) to 24 hours; second maximum about 11 hours; minimum between 17.25 hours (5.15

P. M.), and 18.5 hours (6.30 P. M.), and another between 5 hours and 5.5 hours. Hardly less interesting than these variations in the ionization is the difference in the amount of the charge on the quadrants on the first charging up, and that attained at any subsequent time during the continuation of an experiment. For the combination aluminum within brass the charge reached a maximum of 1.43 volts, and the highest value subsequently attained was only about .25 of a volt. The charge was negative. The observations from which the curves were drawn are given in the accompanying table of observations.

LEAD IN BRASS.

The first part of the curve for lead in brass, Fig. 4, presents an interesting variation from the form of the curve for other combinations of metals. Instead of falling off almost altogether and then

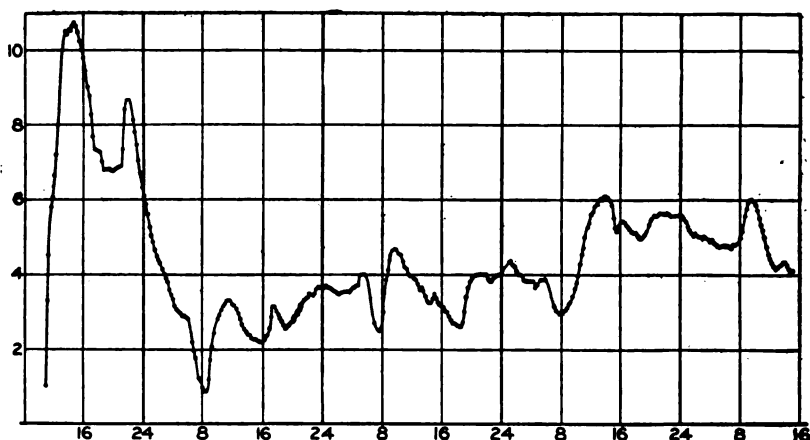


Fig. 4.

increasing, this curve shows that the leak decreased for from 4 to 5 hours, and then increased rapidly for a time, finally falling to a minimum, as is usual in 18 to 20 hours. It is worthy of note that this variation took place about the twenty-fourth hour, or the hour of midnight, at which time all the curves show a maximum. Besides this irregularity the curve shows two other striking peculiarities. One is the constancy of the minimum for each day at about the eighth hour, and the other, the so-called notched maximum, about midnight. If we disregard the first part of the curve and consider

only the portion given for complete days, we see that these midnight maxima are not the principal maxima as in the curves for aluminum in brass. The principal maximum in this curve comes at the time of the secondary in the former curve. The general outline of the two, however, are very like, and the variation is no doubt due to the increase in the amount of leak. As in the preceding curve, so here we find maxima for each day whose time of occurring varies from two to three hours. For lead in brass one variation of the maximum for successive days is from 22.5 h. to 24 h., and the other from 10 h. to 13.5 h. The minimum vary between 20 h. and 21 h. for one, and 7 h. and 9 h. for the other. If we consider the first part of the curve we have further evidence for the existence of the

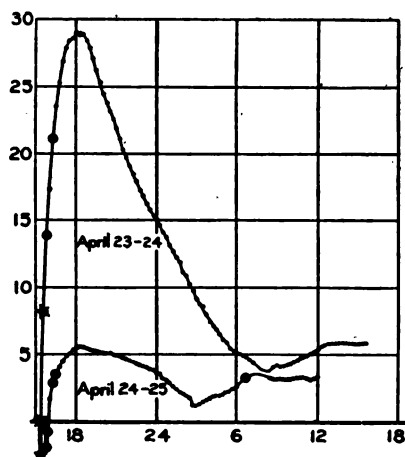


Fig. 5.

maximum between the twenty-second hour and the twenty-fourth. In this curve the progressive increase in the ionization is very evident, as it is in all the curves where one of the cylinders is of lead, and indicates that this steady increase is due to some property of the metal.

LEAD IN LEAD.

The leak between a lead cylinder, and another of the same metal, was, in these experiments, so surprisingly great, that an effort was made to determine its source. Accordingly after the leak had fallen off, and had become comparatively constant, the inner cylinder

and the quadrants were disconnected and earthed. After about half an hour they were again insulated, and a new set of readings begun. The curves drawn for the two periods show the same general form. The rise in the second case, however, falls short of that attained in the first, and indicates that the ionization is due to a radio-active deposit on the surface of the metal, whose activity dies out with time. For both sets of readings the curves show that the maximum was reached in the same time, but in the second case the fall is less rapid. Since the time of fall in this case is almost coincident with the time of the principal maximum daily variation, we

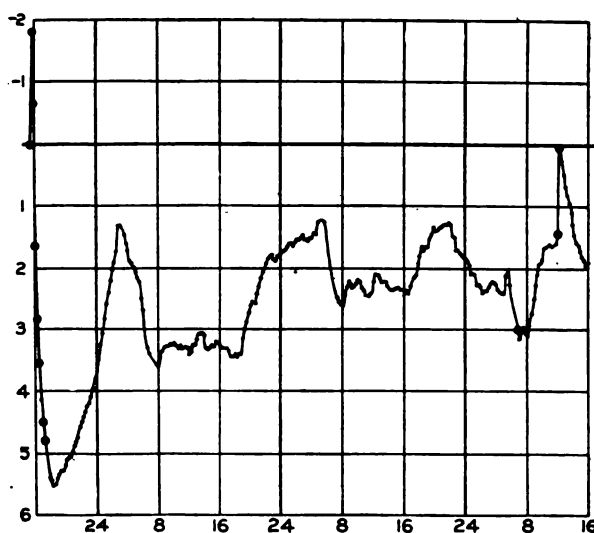


Fig. 6.

may attribute the retardation of the fall to whatever produces this variation. The observations from which this second curve was plotted, with subsequent observations are replotted in Fig. 6, in such a manner that the downward direction indicates a positive charge. The result of grounding the inner cylinder after the first twenty-four hours, and beginning a new set of observations is here clearly seen in a loss of definiteness in the periodic character of the curve. It is true, that we find maxima and minima at about the same hours at which they occurred in the curves previously given, but they are less clearly defined. If we consider full twenty-four

hour periods from one hour we find a maximum for each day for which the curve is drawn, at 22.5 h. Most evident of all, however, is the morning minimum, occurring as it does at 8 h. on three successive days. The afternoon fall though less evident is clearly defined and occurs as usual about the sixteenth or seventeenth hour. It must be pointed out, however, that two of the maxima observed do not come at a time at which maxima are usually observed, and that the two very great fluctuations observed at a time somewhat later than the usual time of the night maxima seem to be connected with weather conditions, for a storm was on at the time, and it has been invariably observed that a violent rain storm produces a marked increase in the deflection of the needle always in the direction indicating a negative charge.

ALUMINUM IN LEAD.

The observations from which this curve for aluminum in lead, Fig. 7, was drawn were taken after the central cylinder had been

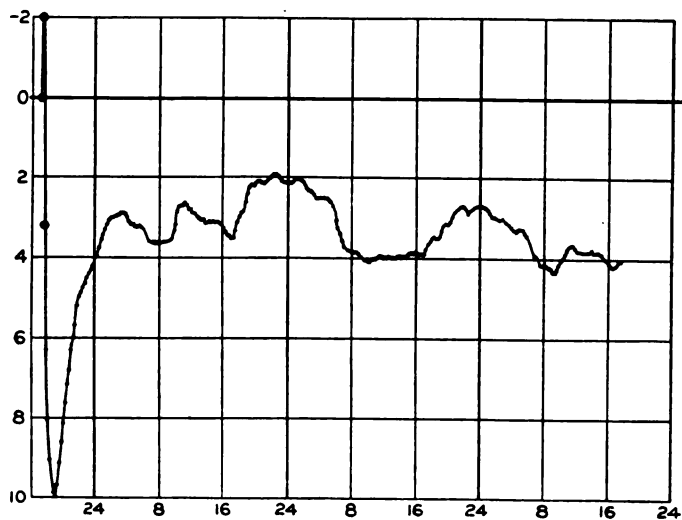


Fig. 7.

connected to the quadrants, and insulated for twenty-four hours. At the end of this time the quadrants were earthed and, after a brief interval, insulated again, and a new set of readings begun. The

curve for the first period is not given, as the first part of this curve corresponds with it in outline. The activity of this combination of metals was very great, the maximum deflection indicating a potential difference of over 2 volts. The curve is noticeable for the likeness it bears to the other curves where lead was the metal of the outer cylinder. To point out this likeness is of some importance since it indicates that the metal of the outer cylinder modifies, to some extent, the results obtained. As plotted the downward direction indicates the deflection corresponding to a positive charge and shows that there is a gradual increase of the charge from day to day. It will be noticed in these curves that the maximum and minimum are not preceded and followed by a rapid rising and falling of the curve, but that the maximum continues fairly level throughout the night, and the minimum throughout the day. Even so it is possible to recognize the usual maximum occurring from the twenty-second to the first hour, and a second maximum between 10 h. and 12 h. Minima occur between 16 h. and 18 h. and between 6 h. and 9 h.

BRASS IN LEAD.

Observations with this combination of metals, Fig. 8, were continued for a somewhat longer time than in the preceding experiments with the hope that most convincing evidence of the regularity of the

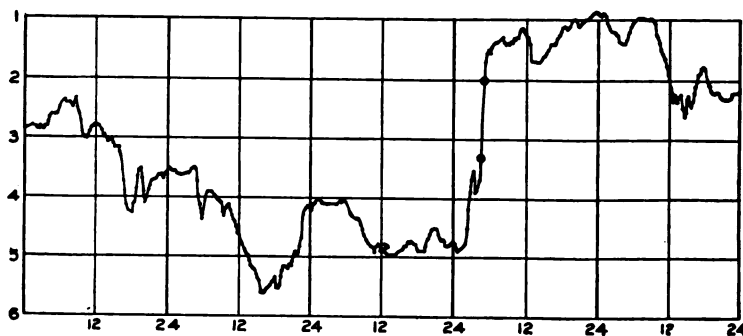


Fig. 8.

maxima and the minima would be obtained. However, the progressive change in the amount of ionization and in meteorological conditions, which undoubtedly have an influence, has broken up the

regularity somewhat, and on one day at least evidence of maxima and minima is not clearly defined. The curves, moreover, never indicate clear-cut maxima and minima quite satisfactorily when the deflection indicates a positive charge on the free quadrants. Except on one day when there was an unusually large variation which was coincident with a heavy rain storm accompanied by thunder and lightning, the time of occurrence of maxima and minima is in fair agreement with the results obtained by Wood and Campbell. Maxima occur at a time varying between 22 h. and 2 h. for the different days, and morning maxima varying between 7 h. and 9 h. The principal minima occur with great regularity between 14 h. and 18 h., and secondary minima may be recognized between 2 h. and 5 h. In general the results obtained with this combination of metals is in agreement with the results previously obtained, yet there are differences which suggest that the influences which bring about the variations are modified in their action by the nature of the metals used, and especially by the metal of the outer vessel. This supposition is strengthened by its general likeness with the other curves where the outer cylinder is of the same metal.

TIN IN TIN.

This experiment was made merely for purposes of comparison with the results from other experiments, and to verify the order of activity of the metals, lead and tin, given by Strutt and others. This order is confirmed by the results obtained, lead having been found much more active than tin. A quantitative comparison was not attempted as it was next to impossible on account of the differences in experimental conditions.

DISCUSSION OF RESULTS.

Some of the results obtained in these experiments are not in agreement with those obtained by McLennan and Burton. For example, they found, for all the metals tried, that if the cylinders

¹ At the end of this experiment it was found that the zero had changed considerably. An effort was made to trace the cause. For this reason the apparatus was left intact for several hours. In about 12 hours a drift toward the original zero of 5 mm. was noted. Later the needle and quadrants were earthed then insulated, and a drift of 5 mm. noted in two hours. This would seem to indicate that the quartz fiber had suffered fatigue under the continued strain.

were of the same metal, the inner cylinder acquired a negative charge, whereas for the two metals, lead and tin, which I have tried, the inner cylinder acquired a positive charge. McLennan and Burton thought that the negative charge acquired by the cylinder resulted from a process in which an excess of positively charged corpuscles was expelled from its surface. At first sight it seems impossible to reconcile my results with those they have obtained, but if we consider that the discharge is due to some agent on the surfaces of the cylinders, or to a radiation from the surface of the metal itself, then the inconsistency may be explained away. In either case the amount of radiation should be proportional to the area of the surface of the cylinders. Hence if the cylinders are nearly of a size the amount of radiation from each will be about the same. On the other hand, if the cylinders are of quite different sizes then a much greater number of corpuscles will be shot off from one than from the other, and the cylinder from which the greater number is shot off will become negative with respect to the other. In McLennan's experiments the area of radiation does not greatly differ for the two cylinders, while in the experiments described in this paper the effective area was quite different. If now we suppose that the negative charge of the earth has a restraining influence on the escape of the positive corpuscles, the leak from the inner cylinder, which is insulated, will start first, and the two cylinders will act like a galvanic battery, with the inner cylinder as the negative pole and the air as a dielectric. The direction of the field thus created will have a retarding influence on the corpuscles from the outer cylinder, and more of them will be absorbed in their passage through the gas than if this field did not exist. If this absorption is sufficient to overcome the excess of corpuscles from the outer cylinder in McLennan's experiments, but not sufficient in the experiments herein described, then the two results are reconciled. Moreover, this interpretation not only reconciles the two results, it also enables us to explain why all the curves which ultimately indicate a positive charge show that at the start there was a deflection in the negative direction. The length of time of this negative deflection gives us a means of determining the strength of the retarding influence exercised by the earth's field, and by the leak between the cylinders. Furthermore,

the smallness of the negative charge measured by McLennan shows that the absorption was barely sufficient to overcome the excess of corpuscles from the outer cylinder. Further experiments will be made to test the soundness of this view.

To assign a cause for the periodicity of the ionization in a closed vessel, in the present state of our knowledge of the subject, is to present what must be considered more or less probable, and what must remain so until experiments have been made in widely different parts of the world. At best the explanations put forth, as in all cases where new ground is broken, must be looked upon as working hypotheses. So it is with the explanation offered by Wood and Campbell, and the one favored in this paper. Wood and Campbell trace a connection between the periodicity and the potential of the atmosphere, and give comparative ionization and potential curves for several consecutive months. These curves do, indeed, show a decided similarity, yet that Wood and Campbell themselves are not altogether satisfied that this seeming interdependence fully explains the phenomena is implied in their cursory reference to another possible cause.

One explanation of the phenomena that readily suggests itself is that the periodicity is due to the ionization which is known to be present in the atmosphere and indirectly to whatever produces this ionization.

Several observers have shown that radium and thorium emanations exist in the atmosphere, and Elster and Geitel have made a detailed examination of the effect of meteorological conditions on the amount of excited radio-activity to be derived from this source. A large number of observations were taken extending over a period of twelve months. They found that the amount of excited activity obtained was subject to great variations. Yet no evidence is given to show that these were periodic in character. No direct connection could be traced between the amount of ionization in the atmosphere and the amount of excited activity produced. More recently Dike¹ has obtained some evidence, which tends to show that there is a daily variation in the amount of radium emanation in the lower regions of the atmosphere. He found that the induced radio-activity depos-

¹ *Terrestrial Magnetism*, Vol. II., No. 3, p. 128.

ited on a negatively electrified surface in the Cavendish Laboratory has diurnal periods with a well-marked maximum at 1 A. M. Dike's observations, however, were continued only through six days. Similar diurnal variations in the amount of induced radio-activity have also been observed by Simpson² in Lapland.

In view of the fact that the theories already put forth to account for the periodic character of the ionization are not wholly convincing, it will not be out of place to consider another source of the ionization. O. W. Richardson¹ has pointed out that the connection between the periodicity in the ionization in closed vessels, and the variation in the intensity of the electric field near the earth's surface may be explained on the theory of conduction through gases if it is assumed that the ionization is caused by radiation from extra-terrestrial sources. The source of this radiation which Dr. Richardson suggests is the sun. Certain of the rays from the sun possess ionizing properties. These rays will be absorbed in passing through the atmosphere, and only the more penetrating will reach the earth. But in proportion as the rays are absorbed, ions are produced, hence the ions from this source will be more numerous in the upper regions of the atmosphere than nearer the earth. If, as Dr. Richardson does, we regard the earth and the upper atmosphere as two plane electrodes maintained at a constant difference of potential, we see that the ionization in the air near the upper atmosphere will be much more intense than near the earth, and hence the potential gradient will be least, for it has been found that where the ionization is to a large extent confined to the volume of air near one electrode, the potential gradient is least in its neighborhood and increases as the other electrode is approached. Thus any cause which brings about an increase in the intensity of the ionization in the upper air will increase the electric intensity near the surface of the earth.

The results of the experiments described in this paper are an indirect confirmation of this view in so far as they give evidence in favor of the source of the earth's electric field, upon which Richardson's conclusions are based. His theory of the origin of the earth's field is that it arises in rainy regions on account of the neg-

¹ Phil. Trans., 205, p. 61, 1906.

² Nature, April 26, 1906, p. 607.

actively charged rain conveying its charge to the earth, which thus becomes negatively charged. This leaves a high positive potential in the atmosphere immediately above the rainy region, which very rapidly distributes itself over the earth's surface by means of discharges in the upper regions of the atmosphere, where the pressure is low enough for ionization by collisions to occur. Owing to the high conductivity of the upper regions of the atmosphere, therefore, the potential will differ only to a relatively slight extent over different regions of the earth's surface; most of the fall of potential between the positive charge over the rainy region and any point on the earth's surface will occur in the badly conducting layer of air at a high pressure, which is comparatively close to the earth's surface. The main point in support of the above view of the origin of the earth's field, derived from the experiments herein described, is the observation, made repeatedly during the course of the experiments, that a rain storm was invariably accompanied by a rapid fluctuation of the charge on the free quadrants. On several occasions the fall of rain was preceded by lightning and thunder, but it was not until the rain began to fall that the rapid fluctuations of the charge took place. The connection between weather conditions and the unusual fluctuation of the charge on the quadrants has been pointed out in the discussion of each particular combination of metals, except for the first part of the experiment with the combination lead in lead, which was carried out while a heavy rain was falling. The observations taken during this period have not been plotted, as the fluctuation of the charge was accompanied by a change in the position of the zero, which rendered the value of the readings very uncertain.

Whatever be the source of the ionization, one thing is evident, the ionization in a closed vessel has a double daily period. Moreover, the uniformity in the time of occurrence of the respective maxima and minima in experiments made in so widely different parts of the world as Cambridge, St. Petersburg¹ and Washington makes the view that the variations are caused by radiation from the sun ionizing the air and thus bringing about a fluctuation in the earth's electric field, appear the most probable explanation of the phenomena.

¹ See Science Abstracts, 1904, No. 1580.

THE ABSORPTION OF HYDROGEN BY METALLIC FILMS.

BY WILL C. BAKER.

PROFESSOR SKINNER¹ has shown that when a discharge is sent, at low gas pressure, to a freshly polished cathode, hydrogen is liberated from the metal initially in the quantities required by Faraday's law for electrolytes. The proportionality between the mass of gas set free per second and the current soon diminishes (if the current be maintained), presumably as the available hydrogen in the surface layers is exhausted; for on standing in a hydrogen-free atmosphere the metal recovers its original power of giving off gas, probably through diffusion from the deeper layers. Heald,² in attempting to measure this absorbed gas by volatilizing the metal in a partial vacuum, concluded that the films thus condensed on the walls of the tube showed a measurable absorption of hydrogen. He states that even with quantities of active metal "too small to measure," a diminution of pressure was observable for an hour or more after the production of the film. Skinner³ had already shown that the cathode in his experiments did not re-absorb the gas that had been liberated from it; but this was possibly due to the more ready absorption of hydrogen (probably atomic) from the interior of the metal. Thus it appeared quite possible — especially in view of Heald's observations — that a film of metal produced in a hydrogen-free atmosphere might show a measurable absorption on being exposed to hydrogen; also that it might be possible to determine the quantity of gas absorbed per gram of metal, if it were a volume effect; or the quantity of gas condensed per unit area if it were merely a surface phenomenon.

To decide these points metallic films of measurable mass were deposited by "spluttering" from a cathode, through a gas that had

¹ PHYS. REV., July, 1905.

² PHYS. REV., March, 1907.

³ *Loc. cit.*

been carefully freed from hydrogen. The apparatus was then allowed to stand for an hour to permit it to cool from any heating arising from the deposition of the film; and finally, a known quantity of hydrogen was forced into the apparatus and the pressure measured from time to time. As the volume employed was less than one tenth of that used by Heald, and as weighable quantities of metal were used, the effect, if it existed under these conditions, would have been easily measurable. It was usually one minute after the introduction of the hydrogen that the first pressure reading was taken; but the pressure obtaining at the first contact of the film



Fig. 1.

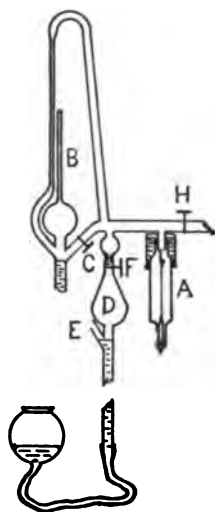


Fig. 2.

and gas could be approximately found from the volume of the apparatus, the pressure before the injection of the hydrogen, and the quantity of that gas used. Thus any absorption occurring in the first minute would have been detected. Cathodes of silver, iron and platinum were used. The two former are metals that gave large values in Heald's experiments. In no case was any absorption detected.

Figs. 1 and 2 give a diagrammatic representation of the experimental arrangements. In order to increase pressure changes the apparatus was kept as small as convenient, the main chamber with

attached gauge, etc., had a volume of about forty cubic centimeters. The cathode consisted of a fine wire seven centimeters long. This was hung from a glass hook as shown in Fig. 1 and was easily weighable before and after the experiment. It was slightly stretched by supporting at its lower end a small piece of capillary tube through which passed an aluminium¹ wire, making connection between the cathode and the fused-in platinum lead through a drop of mercury. This discharge chamber was attached to the rest of the apparatus by a sealing-wax joint, "drowned" in mercury; the latter serving to give it heat capacity, thus preventing the wax from softening during the discharge. The film had a superficial area of about forty square centimeters. The relation of this tube to the rest of the apparatus is shown in Fig. 2. *A* is the discharge chamber. *B* is a McLeod gauge. In order to enable readings to be made quickly, a by-pass with a tap, *C*, connected the main apparatus to the stem of the gauge at a point about a millimeter below the level of the capillary side tube. As this by-pass was about four millimeters diameter, the gauge quickly took up the pressure of the apparatus when the tap was open. In taking a reading the tap, *C*, was closed *just after* the mouth of the by-pass was covered by the rising mercury. The gauge then acted in the usual way. This arrangement gave complete satisfaction. The chamber, *D* (54.5 cc.), with tap *F*, served to give a definite volume of hydrogen and was connected through *E* to a half liter reservoir where that gas was stored over P_2O_5 . A second McLeod gauge, also in connection with *D*, gave the pressure of this part of the apparatus. A fiducial mark was made about a centimeter above *F*, at a constriction in the tube, and the volume between this and *F* was kept full of mercury, forming a seal against hydrogen leaking into the discharge chamber from *D*. Knowing the volume of *D* from the side tube *E*, to *F*; and adjusting the pressure of the hydrogen filling it, a definite quantity of gas could be sent into the apparatus by first raising the mercury so as to close *E*; opening *F*, thus letting the mercury seal fall into *D*; then on continuing to raise the mercury to the fiducial mark the gas was forced into the main apparatus and the tap sealed as before. Between the tap *H*, which limited the

¹ Aluminium does not "splutter" in vacuo.

experimental volume in that direction, and the pump, were attached (1) a bulb containing the liquid alloy of sodium and potassium, (2) a spectrum tube an electrode of which served as the anode of the discharge chamber, and (3) a drying bulb with P_2O_5 . The gauges "magnified" the pressure fifty times. All the taps were lubricated with a mixture of paraffin, vaseline and rubber according to Travers¹ formula.

The experimental procedure was as follows: The discharge chamber and cathode were removed and a closed tube sealed on in their place. The tap *F* being open, the entire apparatus was exhausted by a water pump; then hydrogen² was let in through a tap not shown. This exhaustion and filling was repeated four or five times. The whole apparatus was next exhausted by the Toepler pump to a pressure of about one millimeter. The mercury was raised, filling *D*, and its level adjusted to the fiducial mark. *F* was then closed, and air admitted to the main apparatus. A current of air, entering through the stem of gauge *B* was maintained until the hydrogen had been swept out of the gauge and pump. The discharge chamber and weighed cathode were next put in place and the apparatus filled with nitrogen.³ In the cases of iron and platinum the cathode was made red hot in a nitrogen atmosphere by running the discharge, at a pressure of six one hundredths of a millimeter; and the apparatus was filled with nitrogen four times more, exhausting each time to one millimeter. This gas was allowed to stand for twenty or twenty-two hours in contact with P_2O_5 . After drying, the gas was purified from any remaining hydrogen by running the NaK bulb with the alloy as cathode, until the spectrum of hydrogen had entirely disappeared. A Browning direct vision spectroscope was used. After purification, the film was deposited, let cool for an hour, the hydrogen injected and the readings made. A few hours later the ratio of the volume of *D* to the experimental volume was determined by measuring the increase in pressure produced in the apparatus by the introduction of a definite quantity of gas. This ratio varied from experiment to experiment due to the

¹ The Study of Gases.

² From Zn and HCl, dried by bubbling through strong H_2SO_4 .

³ Prepared as recommended by Travers (loc. cit.) by drawing air from outside the building, through strong NH_3 , then over red hot copper turnings, and finally through two wash bottles of concentrated H_2SO_4 to remove moisture and excess of ammonia.

fact that the sealing-wax joint was seldom twice in exactly the same place.

On account of the small volume employed the well-known effect of the lowering of the gas pressure accompanying discharge was especially prominent during the deposition of the film. In the case of iron five hours were required in this process. Also the NaK alloy absorbs nitrogen as well as hydrogen. This would soon

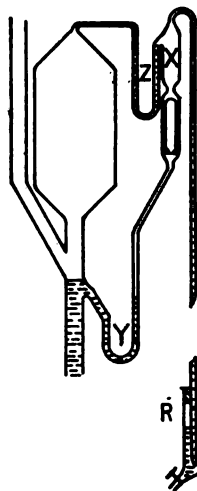


Fig. 3.

increase the vacuum until the discharge would not pass were there not some means of feeding gas back into the tube. To overcome this the valve chamber of the pump was utilized. During the final drying the gas was left at a pressure of about a half a millimeter; the mercury having been turned completely through the pump leaving no gas in the valve chamber *X* (Fig. 3). After drying and purifying, the apparatus was pumped down to the required pressure but the excess of gas was *not turned out of the pump*; it was allowed to remain in the chamber *X*, being kept there by the traps at *Y* and *Z*. If now the mercury in the main stem were lowered below the level of the mouth of the tube *Y*, and if more

mercury were poured into the fixed reservoir at *R* until its surface was less than the barometric height below the bend above the valve chamber, large drops would fall on top of the open valve and slipping down would enclose gas in the tube *Y* and force it over into the pump head and so into the apparatus. This process could be stopped by lowering the mercury in *R*. In this way dried and purified gas could be returned to the discharge tube at will.

TYPICAL MEASUREMENTS. IRON.

Cathode wire well cleaned with sand paper. Heated to bright redness in nitrogen at 4/50 mm. Apparatus refilled four times.

Film deposited at 4/50 mm. after drying and purifying gas. Film a light brown at edges but a black mirror in body of deposit.

Mass of wire before depositing	0.0280 gms.
“ “ “ after “	0.0260 “
“ “ film deposited	0.0020 gms.

54.5 cc. hydrogen admitted to discharge chamber at	32.5 fiftieths of mm.
Gas in discharge chamber before admission of hydrogen at	2.4 " " "
Hydrogen injected at 11 hrs. 06 min. A. M.	
Pressure observed at 11 " 07 "	45.2 fiftieths of mm.
" " 08 "	45.2 " " "
" " 10 "	45.2 " " "
" " 14 "	45.2 " " "
" " 18 "	45.1 " " "
" " 22 "	45.2 " " "
" " 27 "	45.2 " " "
" " 38 "	45.2 " " "
" " 45 "	45.2 " " "
1 hr. 15 " P. M.	45.0 " " "
Ratio of volume <i>D</i> to discharge chamber, etc., 1.29.	
Pressure immediately after injection of hydrogen, calculated,	44.4 " " "

SILVER.

Wire cleaned with sand paper. Film deposited at 3/50 mm. after drying and purifying gas. Film a bright metallic mirror.

Mass of wire before depositing	0.0756 gms.
" " " after "	0.0744 "
" " film deposited	0.0012 gms.
54.4cc. hydrogen admitted at	44.8 fiftieths of mm.
Gas in discharge chamber before admission of hydrogen at	2.4 " " "
Hydrogen injected at 9 hrs. 54 min. A. M.	
Pressure observed at " 55 "	61.0 fiftieths of mm.
" " 56 "	61.0 " " "
" " 58 "	60.8 " " "
10 " 00 "	61.0 " " "
" " 03 "	60.8 " " "
" " 06 "	60.8 " " "
" " 10 "	60.9 " " "
" " 14 "	60.9 " " "
" " 19 "	60.9 " " "
" " 25 "	60.8 " " "
" " 41 "	60.9 " " "
11 " 20 "	60.9 " " "
1 hr. 04 " P. M.	60.8 " " "
2 hrs. 35 "	60.8 " " "
9 " 00 " A. M. (next day)	61.8 " " "
Ratio of volume of <i>D</i> to discharge chamber, etc., 1.29.	
Pressure immediately after injection of hydrogen, calculated	60.2 " " "

PLATINUM.

Cathode boiled in strong nitric acid to remove occluded hydrogen,¹ washed, and dried in filter paper. After first filling with nitrogen the wire was raised to a bright red heat for one minute. During the deposition of the film the current was run to the wire for five seconds then to the NaK alloy for the next five seconds, then to the wire again and so on using the alloy and wire alternately, five seconds each, during the entire period of formation of the film. No trace of the hydrogen spectrum could be detected under this treatment. In other experiments it was found that after the gas had been purified, one could just detect the hydrogen lines when the discharge had run twenty seconds continuously. The film was a mirror, slightly dull owing to the deposition of larger particles during the heating after first filling. Film deposited at 3/50 mm.

Mass of wire before deposit	0.0261 gms.
“ “ “ after “	0.0243 “
“ “ film deposited	0.0018 gms.
54.5 cc. hydrogen admitted at	38.2 fiftieths of mm.
Gas in discharge chamber before admission of hydrogen at	1.2 “ “ “
Hydrogen injected at 11 hrs. 20 min. A. M.	
Pressure observed at “ 21 “	51.7 fiftieths of mm.
“ “ 23 “	51.7 “ “ “
“ “ 25 “	51.7 “ “ “
“ “ 29 “	51.7 “ “ “
“ “ 34 “	51.7 “ “ “
“ “ 40 “	51.7 “ “ “
“ “ 45 “	51.7 “ “ “
12 “ 50 “	51.7 “ “ “
1 hr. 45 “ P. M.	51.7 “ “ “
Ratio of volume <i>D</i> to discharge chamber, etc., 1.31.	
Pressure immediately after injection of hydrogen, calculated,	51.3 “ “ “

The measurements given above indicate that cold metallic films, resulting from cathode deposition, across a hydrogen-free space, do not show a rapid absorption of hydrogen from the molecular state, at least within the limits of accuracy of the experiments recorded in this note.

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QUEEN'S UNIVERSITY, KINGSTON, ONT.

¹ Wilson, H. A., *Phil. Trans. Roy. Soc., A*, Vol. 202, p. 253.

SOME PHYSICAL PROPERTIES OF CURRENT
BEARING MATTER; IV. FRICTION.¹

BY PAUL R. HEYL.

THIS article describes some experiments on the effect of a current upon the friction between a solid and a liquid, the liquid being mercury and the solid either carbon or iron.

For iron, with a current density of about 80 amperes per square centimeter, there is no change in friction as great as one per cent. For carbon, with about the same current density, while there is an apparent decrease of about 14 per cent. with the current, this is entirely accounted for by the accompanying heating effect.

The best method of determining the friction between a solid and liquid is to observe the damping of torsional vibrations when the solid swings in the liquid. If the speed is at all times sufficiently slow, we may assume that the friction is proportional to the speed. On this assumption we have a constant damping factor, or ratio of two successive amplitudes, and the friction is proportional to the Napierian logarithm of this ratio.

When the liquid wets the solid we have, on account of the adhesion of the contact surface, simply the viscosity of the liquid upon itself; but where this is not the case we have in addition the friction at the liquid-solid surface. As already stated, the liquid used was mercury. The metals which are wet by mercury dissolve in it, and we may therefore expect a gradual change in the liquid viscosity where such metals are employed. For this reason, carbon and iron, which do not dissolve in mercury, were chosen. With these substances, the friction, although complex, may be depended upon to be constant.

The form of apparatus used is shown in Fig. 1. A rectangle *AA* of heavy copper wire carried the short rods *BB* of iron or carbon

¹ Earlier articles appeared in *PHYSICAL REVIEW*, XIX., 4 and XXI., 3.

which dipped into the mercury cups *CC*. A current introduced by one of these cups will pass through both sides of the rectangle and leave by the other cup. Several heavy weights *D* served to increase the time of swing to about 25 seconds. The whole arrangement

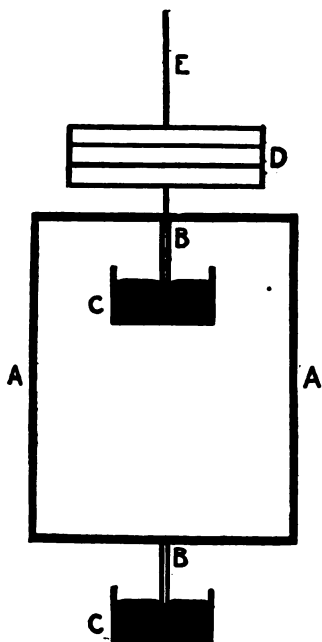


Fig. 1

was suspended by a wire *E* some two meters long, and enclosed in a box with a glass front, the wire *E* passing out by a hole in the top of the box. This wire carried a light pointer which moved over a graduated circle on the top of the box. This circle was printed on cardboard, divided to half degrees, and as its diameter was some 20 cm. it was easily read with a lens to tenths of a degree.

To get as high a current density as possible the rods *BB* were small in diameter, about 3 mm., and dipped very slightly into the mercury. The surface of contact in each cup was about 0.075 sq. cm. With a current of 6 amperes this gave a current density of about 80 amperes per sq. cm. at each point of friction. More

than this could not be used without danger of forming an arc.

It was soon found that the ratio of successive amplitudes was not constant, but suffered a progressive change as the amplitude decreased. Consequently the following procedure was adopted:

The pointer was drawn aside to a certain mark and held there until all swinging of the apparatus had ceased. It was then released and the next three consecutive turning points recorded. From these was calculated the ratio of two successive amplitudes. The first swing was about 60° .

The current was then turned on, and the operations repeated, starting the pointer from the same point. The experiments were thus continued alternately with and without a current.

When carbon rods were used their relatively high resistance

caused a considerable development of heat. They were pieces of electric light carbon, and after a little time became too hot to be touched by the finger. On account of the large amount of mercury in the cups the temperature of the mercury never rose above 35° as measured by a thermometer with a small bulb immersed in the mercury close to the rod. There is no doubt, however, that a very thin film of mercury next the rod was heated more intensely than this.

The effect of the heat upon the viscosity of the mercury may be considered to be eliminated by the alternate method of observing; for the mercury heated by experiment with current had not time to cool more than two or three degrees during the following experiment without the current, and the average temperature of the two sets of experiments was about the same.

We cannot, however, neglect the effect of the heat at the liquid-solid surface. A special set of experiments was made to determine about how much the heating effect might amount to.

The results are given in a condensed form.

Iron-mercury. Current Density, 80 Amperes Per Sq. Cm.		
	Current.	No Current.
Mean ratio of successive amplitudes (40 values)	0.9245	0.9239
Average departure from mean	0.005	0.006
Napierian logarithms of ratios	-0.0786	-0.0792
Difference, about 6 parts in 800.		

Carbon-mercury. Current Density, the same.		
	Current.	No Current.
Mean value of 40 ratios	0.952	0.946
Average departure from mean	0.003	0.004
Napierian logarithms of ratios	-0.0488	-0.0556
Difference, about 7 parts in 50.		

To test the heating effect 15 ratios were measured with no current, the mercury being about 22° . The average ratio was 0.9484 with an average departure of 0.001. The current was then allowed to flow for half an hour, raising the mercury to about 52° . Ratios were measured with the mercury at this temperature, interrupting the current just long enough to measure the two swings necessary for each ratio, and restoring it as soon as that measurement was over. In this way the average temperature of the mercury was kept at about 54° .

Twelve ratios thus measured gave a mean of 0.9613 with an average departure of 0.002. It is thus evident that the effect of the heat at the liquid-solid surface is ample to account for the change observed with carbon, the change here being some 27 per cent. for a rise of about 32° . This is confirmed by the absence of any effect of current upon friction in the case of iron, where the heating effect was negligible.

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THE PHYSICAL REVIEW.

SPECTROPHOTOMETRY OF NORMAL AND COLOR- BLIND EYES.

BY F. L. TUFTS.

I. DEFINITIONS OF THE TERM "EQUAL LUMINOSITY" AS APPLIED TO COLORED LIGHTS.

THE experimental determination of the relative luminosity of the different parts of a spectrum offers very serious difficulties, and, while a number of different types of instruments have been constructed for the purpose of making such measurements, most have shown defects either in the accuracy of the results obtained or in the matter of manipulation. Instruments of the type of the Vierordt double-slit spectrophotometer, or of the Brace spectrophotometer, are of course not of this kind, and while very convenient and accurate for the comparison of the relative luminosity of different sources of light in any given part of the spectrum, give no means of determining the relative luminosity of a given source in the different parts of its spectrum. All instruments for this latter purpose may be conveniently classified under three general types depending upon the definition of the term "equal luminosity," employed for the interpretation of the results obtained when comparing different colored lights. The three definitions most frequently employed are the following :

I. Two similar surfaces, illuminated respectively by two lights of different color, may be said to be of equal luminosity if, in the judgment of the observer, they appear equally luminous.

This definition presupposes in the observer the ability to form a

judgment concerning equality of luminosity, which is not influenced by differences in color. Concerning such judgments, Helmholtz has remarked :¹

"I must explain that personally, I put no confidence in my judgment concerning the equality in luminosity of differently colored surfaces. I admit, however, that of two differently colored fields, one can be so much darkened that there remains no doubt that the other is brighter."

Abney and Festing have constructed and used a spectro-photometer depending, in its action, upon this definition of the term "equal luminosity." By varying the luminosity of one of the surfaces until it appears first more luminous and then less luminous than the other, and taking a mean, they have been able to employ it in some very interesting photometric work.²

II. Two similar surfaces, white, with black markings on them, illuminated respectively by two lights of different color, may be said to be of equal luminosity if, when placed at the same distance from the eye, the details can be distinguished with the same minuteness.

According to this definition, the measure of luminosity is the amount of light, independent of color, which is necessary to enable one clearly to distinguish objects. A method of color photometry depending upon this definition of luminosity was very carefully developed by Maci de Lepinay and Nicati,³ and they showed that the second definition is not always equivalent to the first. This method has been applied to the determination of the relation between energy and luminosity in different parts of the spectrum by Langley,⁴ A. König,⁵ and Pflüger.⁶ A spectrophotometer has been constructed upon this principle by E. S. Ferry,⁷ and used to determine the distribution of luminosity, according to this definition of it, in the light of a 16 candle-power Edison incandescent lamp. He also investigated the relation between luminosity as thus determined and persistence of retinal impressions in different parts of the spectrum.

¹ *Handbuch der Physiologischen Optik*, second edition, p. 440.

² *Color Photometry*, *Trans. Roy. Soc. Lond.*, 1886, p. 423, and 1888, p. 547.

³ *Annales de Chimie et de Physique*, 5th series, vol. 24, p. 30.

⁴ *Am. Jour. Sci.*, 36, pp. 359-380, 1888.

⁵ *Z. Psy. Phys. d. Sinnesorgane*, 4, pp. 241-348, 1893.

⁶ *Ann. d. Physik*, 9, pp. 185-208, 1902.

⁷ *Am. Jour. Sci.*, 44, pp. 192-207, 1892.

III. Two similar surfaces, illuminated respectively by two lights of different color, are said to be of the same luminosity if, on rapidly replacing one by the other before the eye, there is no sensation of flickering. Methods of color photometry depending upon this definition of equal luminosity have been developed by Rood,¹ Whitman² and Tufts.³

It has been shown experimentally that the luminosity, as thus defined, of a white or gray light formed by combining two or more colored lights, is equal to the sum of the luminosities of the colored lights so combined. The writer is not aware that the second definition has been subjected to such an experimental test.

A new form of spectrophotometer for the measurement of color luminosities according to definition III., is described in the present paper, and the results are given of measurements of the luminosities of the different parts of the spectrum as they appear to normal and to color-blind eyes.

II. DESCRIPTION OF THE FLICKER SPECTROPHOTOMETER.

The instrument consists of a spectroscope, Fig. 1, in which the telescope *T* and the axis of the rotating sectored disc *D* are rigidly

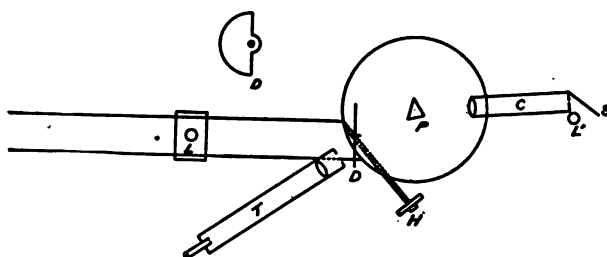


Fig. 1.

fastened to a table, while the collimator *C*, the prism *P*, the lamp *L'* and the white screen *S* are rigidly connected with the graduated circle of the spectroscope. This circle, together with the connected parts, can be rotated about a vertical axis through its center by means of a screw with a graduated head *H*. The light *L* is

¹ *Am. Jour. Sci.*, September, 1893, September, 1899, October, 1899.

² *PHYSICAL REVIEW*, vol. 3, no. 4, 1896.

³ *Trans. N. Y. Acad. Sci.*, XVI., April, 1897.

mounted on a photometer bar so that its distance from the white rotating disc D can be varied, and thus vary the luminosity of the disc. The disc D and the screen S are covered with white paper cut from the same piece. The eye-piece of the telescope is provided with a slot of adjustable width. Finally, the instrument is provided with black screens and diaphragms so placed that the photometric measurements can be made in a lighted room.

The adjustment and operation of the instrument are as follows: The lamp L' and the screen S , having been replaced by a Bunsen burner, the flame of which is colored with suitable salts, the spectroscope can be adjusted for minimum deviation of the sodium lines, and the screw H calibrated in terms of the wave-lengths of the light used. The lamp and screen may then be replaced, and the motor which rotates the disc D started. Through half of the revolution of this disc, the slit in the eye-piece is illuminated by the light from the lamp L which is reflected from the disc, while through the remaining half of the revolution it receives light of a given wave-length from the spectrum of the lamp L' reflected from the screen S through the colimator and prism. The speed of the motor rotating the disc D should be adjusted so as to give the best conditions for flickering in case there is any difference in the luminosities of the two lights. The distance of the lamp L from the disc can be varied until all flickering disappears, and the distance measured. By means of the screw H , any part of the spectrum can be made to illuminate the eye-piece slit, and its luminosity measured in terms of the luminosity of the white disc. The relation between the wave-length of any particular color and its luminosity (definition III.), in terms of the observer's white, can be plotted, using wave-lengths as abscissa, and luminosities as ordinates. The curve thus obtained will be referred to as the *wave-length luminosity curve* for the particular observer with the lights used.

Other means of adapting the flicker principle to a spectrophotometer were tried, but none proved so satisfactory as this, particularly for the testing of untrained observers. The writer has found that any person at all accustomed to looking through optical instruments, such as microscopes or telescopes, can obtain very uniform readings with this form of spectrophotometer, without any preliminary

training. By using a method of recording the distances of the lamp *L* from the disc, on a fillet of paper, described by Professor Rood,¹ the average observer can take ten readings for each of eight or ten positions in the spectrum, in from 20 to 25 minutes, and without any fatigue more than would be experienced in using a microscope or telescope for the same length of time.

III. PHOTOMETRIC MEASUREMENTS WITH THE WRITER'S EYES.

The spectrophotometer just described was employed to investigate the relation between the luminosity of a white and the sum of

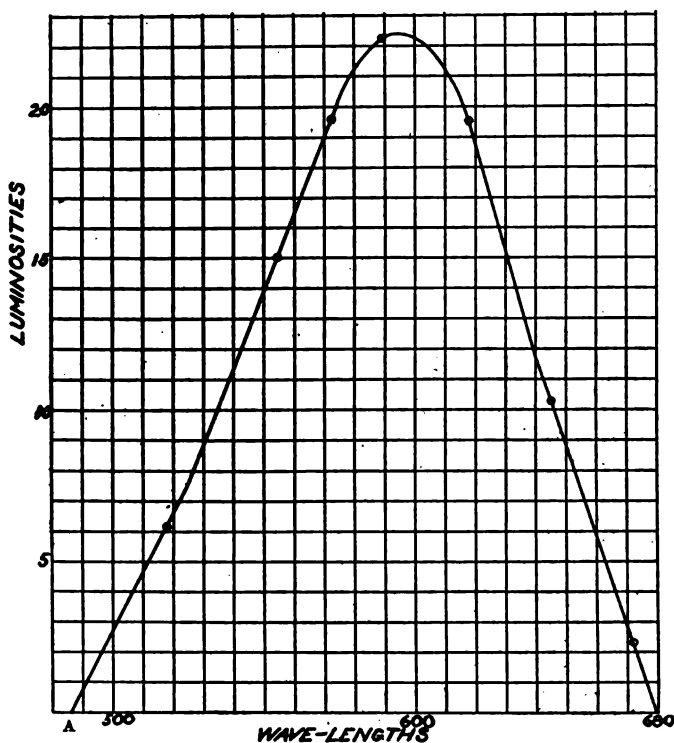


Fig. 2.

the luminosities of its constituent spectrum colors, according to definition III. of the luminosity of a colored light. The writer's wave-length luminosity curve for the reflected light from the lamp *L'* was determined. Each of the points recorded in Fig. 2 is the mean

¹Amer. Jour. Sci., September, 1899.

of from ten to twenty readings. The prism P , Fig. 1, was then removed, and the colimator, together with the attached screen S and lamp L' , turned into such a position that the image of the colimator-slit coincided with the slit in the eye-piece. The luminosity of the white slit was then measured in terms of the same white as was used in the measurement of the luminosities of the spectrum colors. The width of the image of the colimator-slit was measured in terms of the revolution of the micrometer-screw H , the extent of the spectrum between the positions A and B , Fig. 2, having been previously determined in terms of the same unit.

Following are the results of the measurements made :

Luminosity of the image of the white colimator-slit, in terms of the unit used in the wave-length luminosity curve, Fig. 2.....	395
Width of image of colimator-slit in revolutions of the screw H	0.15
Length of spectrum between A and B , Fig. 2, in revolutions of the screw H	4.80
Length of spectrum in terms of width of image of colimator-slit.....	32
Total spectrum luminosity = $\int_A^B \text{lum. } dl$ (where l is expressed in slit-widths) = area between the wave-length luminosity curve and the axis of abscissæ.....	408

One sees that the sum of the luminosities of the spectrum colors determined in this way is equal to the measured luminosity of the original white to within about 3 per cent., which is well within the error of spectrophotometric measurements. Other independent measurements gave similar results, the measured luminosity of the white being sometimes greater and sometimes less than the computed sum of the luminosities of its spectrum colors.

The above results are readily explained if we assume that there is, in the retina of the eye, a sense organ (we will call it the luminosity sense), which is affected in the same way by all visible radiation. The difference between the action of different wave-lengths upon this organ we will assume to be a difference in the magnitude, only, of the effect, and not in its quality.

Since in these experiments the luminosity of any color is measured in terms of the luminosity of the white of the particular observer, any change in the relative luminosity of the different spectrum colors as seen by this observer would not affect the relation of equality between the luminosity of the white of the observer and the sum of

the luminosities of its spectrum colors as seen by him. In other words, no matter how much one may change the quality of one's white, as, for example, by looking through colored glass, the luminosity of that white should always be equal to the sum of the luminosities of its spectrum colors if they also are seen through the same colored glass. Consequently, the area of the wave-length luminosity curve should be the same whether determined by using the naked eye or by making all of the observations through colored glasses, provided (and this must be carefully noted) that the distribution of luminous energy in the spectra of the two lights L and L' is the same.

With the lamps L and L' of different candle power, it is very difficult to obtain the same relative distribution of luminous energy in the two spectra. The lamps used by the writer were the ordinary 50 C.P. incandescent stereopticon lamps. These lamps were tested in the following manner: Two lamps, one at L and one at L' were adjusted for no flickering when the photometer was set in the red, the distance of the lamp L from the disc D being noted. The lamps were then interchanged and the adjustment repeated. The ratio of the luminosity of the red of one of the lamps to the luminosity of the same red of the other lamp was thus obtained. This ratio was also determined for the yellow-green and the blue of the spectrum. Unless the ratios were approximately the same, the lamps were rejected and others compared. After a number of such comparisons, two lamps were found for which the ratio did not differ in different parts of the spectrum by more than 8 per cent. of its mean value. These two lamps were used for the purpose of determining the wave-length luminosity curve for: I. The naked eye; II. The eye looking through a yellow glass; III. The eye looking through a red glass; IV. The same eye looking through a very pale blue glass.

The four curves are plotted in Fig. 3. The crosses indicate the readings for the naked eye, the letters Y , R , and B , the readings for the same eye when looking through the colored glasses respectively. Measurements on the four curves showed them all to have approximately the same area.

When a deep cobalt blue glass was used which transmitted only

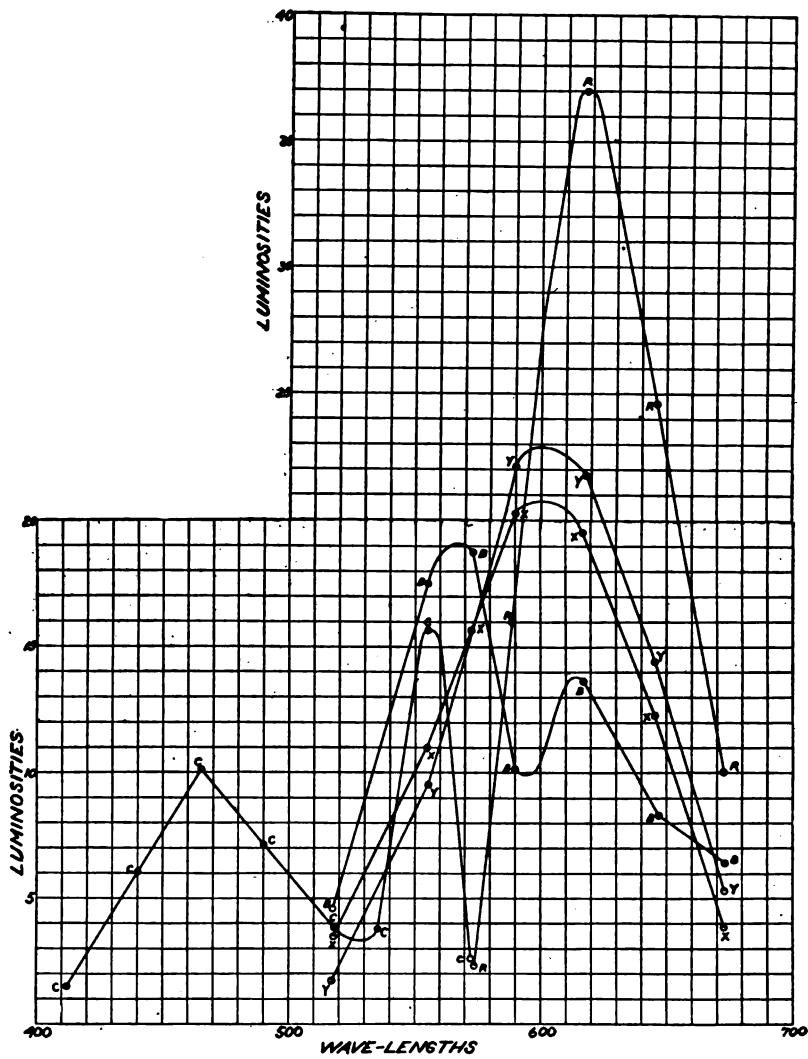


Fig. 3.

the extreme violet end of the spectrum, with a negligibly small amount of light in the red, the results were quite different. The wave-length luminosity curve for an eye looking through the cobalt glass is indicated in Fig. 3 by the letter *C*. If the area of this curve is compared with the area of the naked eye curve, it will be found to be almost 50 per cent. less. When the prism was removed

and the luminosity of the image of the colimator-slit determined by observations taken through the cobalt glass, the luminosity was found to be the same, within 2 per cent., as the luminosity determined by observations with the naked eye. It might seem, therefore, that for an eye looking through cobalt glass, the luminosity of the cobalt-eye's white was greater than the sum of the luminosities of its spectrum colors (def. 3). The phenomenon is possibly connected with the Purkinji effect and is still under investigation. The importance of this in the interpretation of the results obtained from observations with certain abnormal eyes is pointed out in the latter part of this paper.

The practical independence of our color and luminosity sensations is shown by the following experiments. It is well known that if one eye is exposed to a strong light through a green glass, for example, until the retina becomes fatigued, all objects appear to that eye as they would appear to the normal eye if it were looking through a red glass, transmitting a complementary color to the green. The color sense becomes fatigued by exposure to a given color, and it then reacts to stimuli in a way qualitatively different from the unfatigued sense. If our luminosity sense is independent of our color sense, and if its reaction is qualitatively the same for all wave-lengths within the visible spectrum, then it ought to be impossible to change the apparent luminosity of any color (measured in terms of the luminosity of the white of that eye) by fatiguing the luminosity sense of the eye with light of that particular color or its complementary. In other words, the wave-length luminosity curve for the fatigued eye should be identical with the wave-length luminosity curve of the unfatigued eye.

This assumption was tested experimentally in the following way: The wave-length luminosity curves were determined for the writer's two eyes, and were found to be practically identical. The right eye was then exposed to the light of a 100 C.P. incandescent lamp viewed through colored glass, the exposure being of sufficient duration to cause all white objects seen with the fatigued eye to appear of the complementary color to the light transmitted by the glass. The luminosity of a given spectrum color was then measured with the fatigued eye, and, immediately after, remeasured with the un-

fatigued eye. This was done for seven different positions in the spectrum. The right eye was refatigued just before each set of readings, and, in every case, the effect of the fatigue was of sufficient duration to give the complementary color effect after the set of readings had been taken.

The readings with the right eye fatigued by blue light were compared with the readings of the left, unfatigued eye, and the results

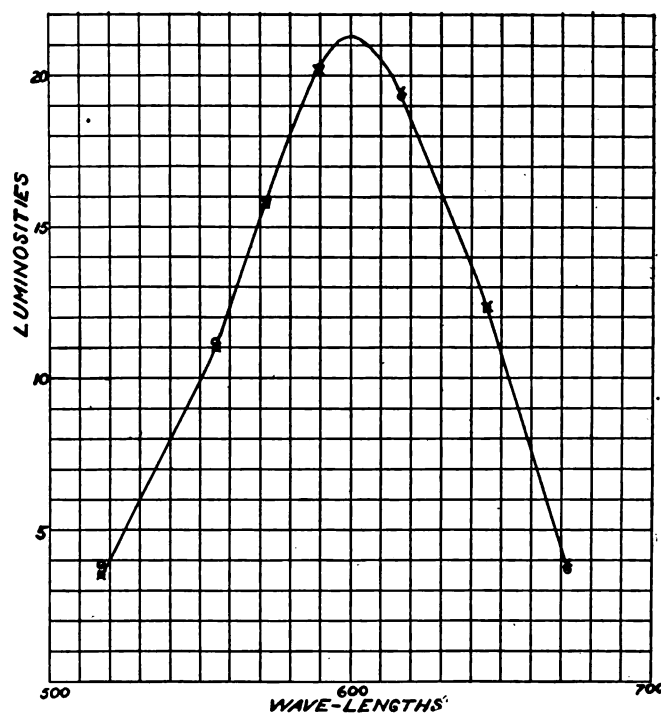


Fig. 4.

are given in Fig. 4. The crosses indicate the readings with the unfatigued eye, the circles, the readings with the fatigued eye. In every case the difference was found to be within the experimental error. Similar results were obtained by fatiguing the right eye with yellow and green lights. In every case the right eye was fatigued by looking at the incandescent filament through the colored glass, the eye being placed so near the filament that the area of the retina

covered by the image was many times the area covered by the image of the slit in the eye-piece of the spectrophotometer.

When a red glass was used (the same piece as was used for the red curve in Fig. 3) and the exposure only sufficient to produce the complementary color effect, the results obtained were similar to those obtained with the other colors. A continuous exposure, however, of several minutes, gave photometric readings with the fatigued eye which were very different from those with the normal eye. The

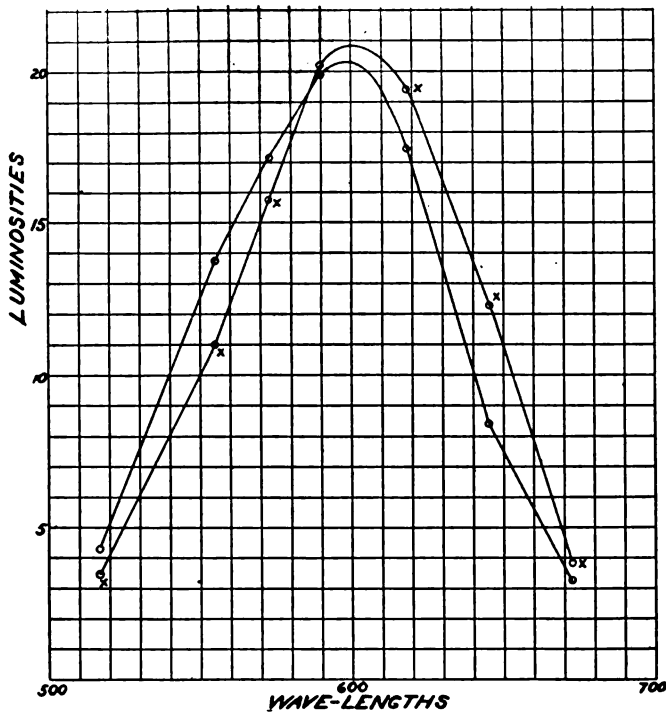


Fig. 5.

general character of the differences is shown in Fig. 5, the crosses indicating the curve for the normal eye, and the circles without crosses the readings for the fatigued eye. An inspection of the figure shows that the effect of a prolonged exposure of the retina to the long, or red rays, is to displace the maximum of the wave-length luminosity curve towards the blue end of the spectrum. This displacement is apparently due to some action of the long waves upon the lumi-

nosity sense, and is either not connected at all, or at least only indirectly, with their action upon the color sense, for the photometric readings became the same for the fatigued as for the unfatigued eye long before the vivid green after-image had disappeared.

The right eye was then fatigued by looking at the 100 C.P. lamp directly, so that vivid, colored after-images were seen as the eye recovered. The photometric readings were, however, the same for the fatigued as for the unfatigued eye. The fatigued eye was always focussed, in taking the readings, so that the image of the slit in the eye-piece was in the center of the after-image of the spiral lamp-filament. The photometric readings, however, did not change, although the background formed by the after-image changed its color as the eye recovered from its fatigue.

The above experiments show that the relative reaction of the luminosity-sense to white light and to light of different colors is not affected by ordinary fatigue produced by exposing the eye to colored or white light, but may be altered by prolonged exposure to red light. Two other persons possessing normal color vision have been kind enough to subject their eyes to the rather harsh treatment required by these experiments, and the results were, throughout, similar to those obtained from the writer's eyes. A change in the relative reaction of the luminosity sense to white and to colored lights was produced only by prolonged exposure to red light, exposure to yellow, green, blue, or white light, and moderate exposure to red, producing no similar effect.

IV. COMPARISON OF THE WAVE-LENGTH LUMINOSITY CURVES OF DIFFERENT EYES.

A number of different persons were kind enough to give the time required for the determination of their wave-length luminosity curves by the flicker spectrophotometer. Some twenty persons in all were examined, an effort being made to secure as many color-blind persons as possible, so that out of the twenty, six showed, by the ordinary Holmgren test, marked red-green blindness (the reds, greens, and grays, being confused in the sorting of colors). Of the fourteen persons possessing normal color-vision, according to the Holmgren test, ten showed a wave-length luminosity curve which

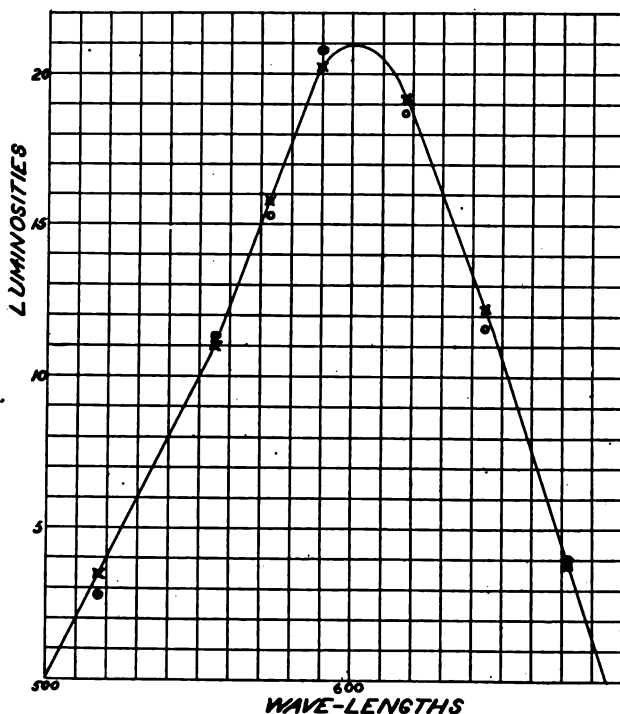


Fig. 6.

differed only slightly from the writer's curve. Representative readings for one of these observers are given in Fig. 6. The crosses indicate the writer's readings, and the circles the readings of one of the ten observers. The results, in both cases, are the mean of ten observations in each position in the spectrum.

Four of the persons studied showed a wave-length luminosity curve differing only slightly from the writer's, but the deviations were all in the same general direction, and seemed to indicate a rather distinct type of curve. One of these curves, which is representative of the four, is given in Fig. 7, and for comparison the writer's curve, indicated by crosses, is also given. The luminosity-sense of these persons seems to be less responsive to yellow, and correspondingly more sensitive to red and violet light, than the normal, thus giving a slightly flattened wave-length luminosity curve. All four persons seem to possess perfectly normal color vision.

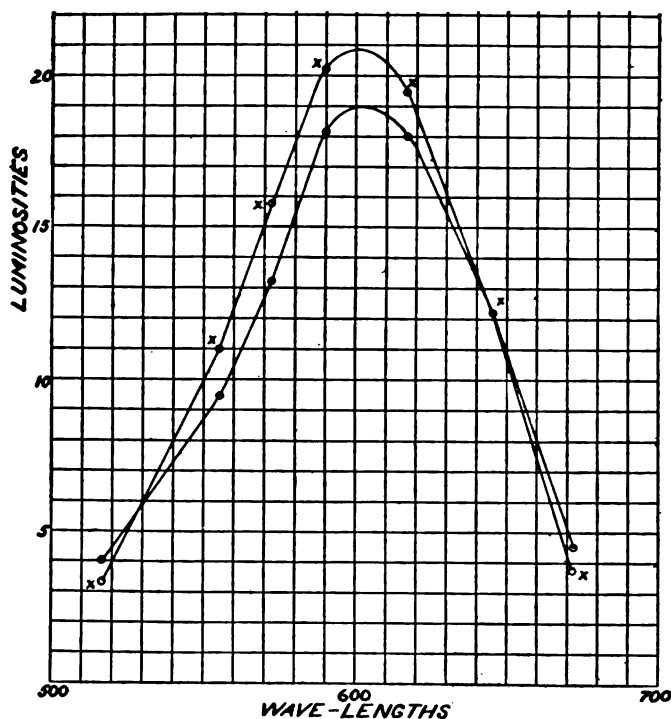


Fig. 7.

Two persons examined showed curves differing very much from the writer's. One of these, and it is almost identical with the other, is given in Fig. 8, the writer's curve being again indicated by the crosses. It is seen that the observer is more sensitive to red and less sensitive to green and blue than the writer. In other words, his wave-length luminosity curve is displaced toward the red end of the spectrum, with respect to the writer's curve. Neither of these persons made any mistake in sorting ordinary colors, but when asked to sort some extremely pale shades, both showed a slight tendency to confuse the oranges and yellow-greens.

Two other observers, both possessing perfectly normal color-vision as shown by the Holmgren test, with pronounced and also extremely pale shades of colors, gave wave-length luminosity curves that were displaced toward the green, with respect to the writer's curve. The curves also showed the peculiarity of having an area

distinctly less than that of the writer's curve. These two persons were kind enough to give the time necessary to repeat the complete set of readings on several different days; and the readings of each set were found to agree, within a few per cent., with the corresponding readings of any other set. The readings for the observer showing the greater deviation from the writer, are indicated in

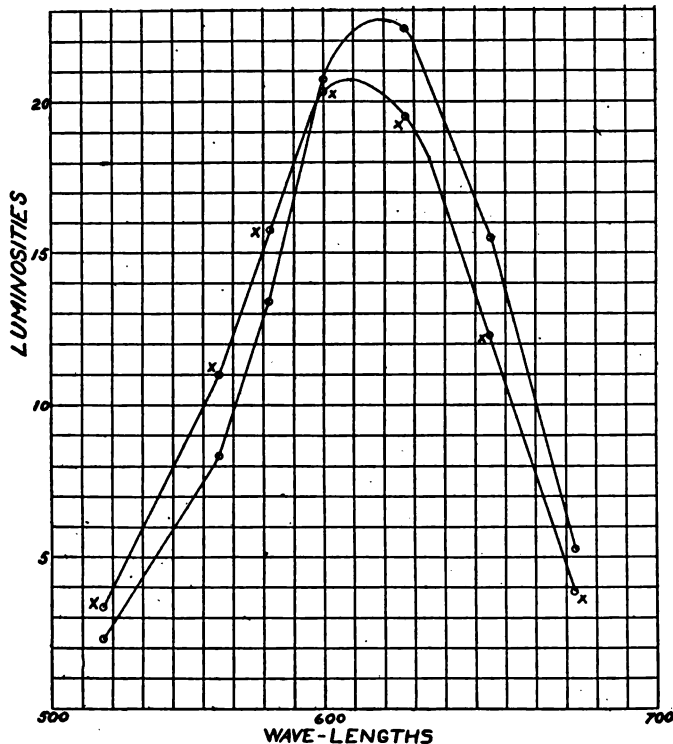


Fig. 8.

Fig. 9 by the circles, the writer's curve being indicated by the crosses. The position of maximum luminosity is seen to be displaced by a very considerable amount toward the green, and the area of the curve is less than the area of the writer's curve by as much as twenty per cent. The curve for the other observer is indicated by the dotted line in Fig. 9. The blue end of the spectrum must supply a much larger per cent. of the luminosity of the white of these observers than is the case with the normal eye, and

the smaller area of the curves might be expected after the observations with the cobalt glass described in part III. of this paper.

The observer whose curve differed most from the writer's curve, in Fig. 9, was also tested by the ordinary flicker photometer with

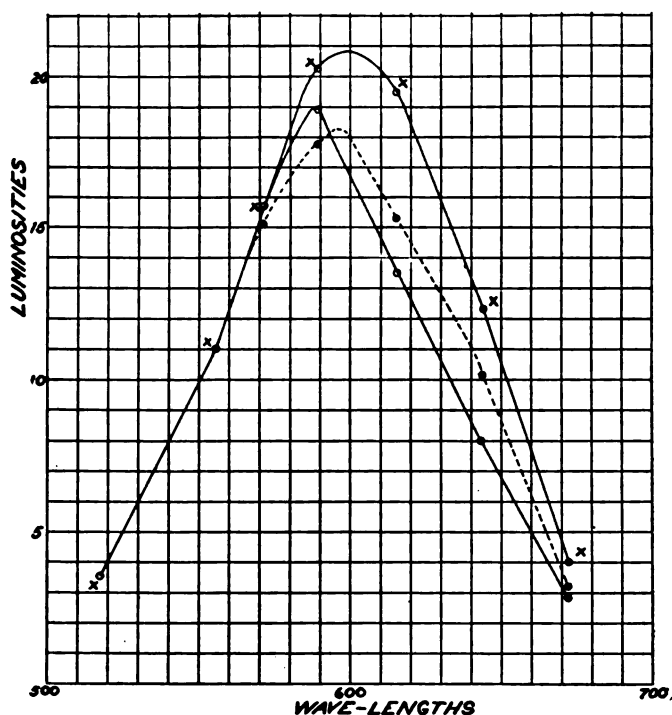


Fig. 9.

colored glasses, the method being the same as that employed by Professor Rood.¹ The results, expressed in terms of the same standard as that employed by Rood, are as follows, for the writer and the observer mentioned above :

Observer.	Apparent Luminosity of the Color.		
	Red.	Green.	Blue.
Rood's normal eye	100	100	100
Writer's eye	90	100	88
Observer's eye, Fig. 9	36	100	87

¹On Color Vision and the Flicker Photometer, by Ogden N. Rood, *Am. Jour. of Science*, Vol. VIII., October, 1899.

It is therefore evident that an observer may be abnormally weak in the luminosity impression produced by a given color of light, and still be perfectly normal with respect to color sensations.

Six persons, all showing very marked red-green color-blindness by the Holmgren test, very kindly offered to give the time necessary for the determination of their wave-length luminosity curves. All

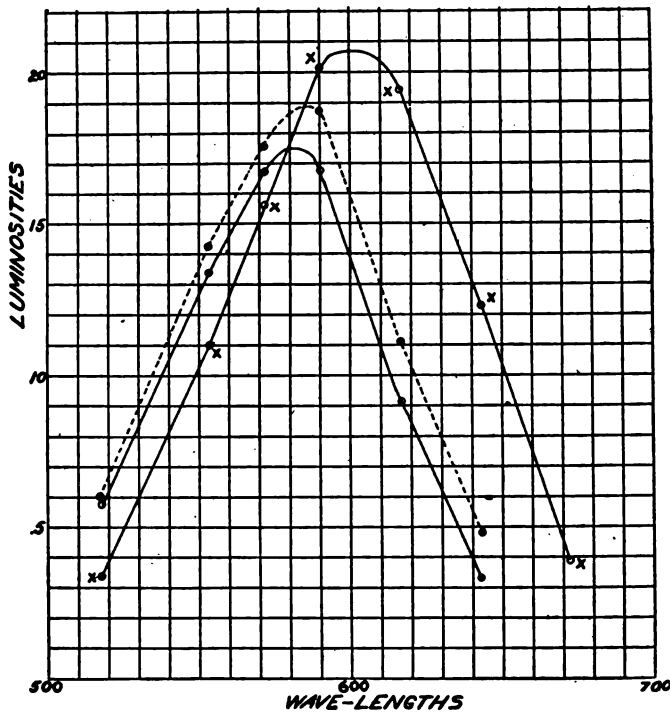


Fig. 10.

six persons confused the reds, greens, and grays, in the sorting of colors. Of the six persons, three were found to have wave-length luminosity curves in which the point of maximum luminosity was displaced towards the green, while the other three showed a displacement towards the red.

Of the first three curves, the one differing most and the one differing least from the writer's curve are given in Fig. 10, the writer's curve being indicated by crosses. All three of the curves had a much smaller area than that of the writer's curve, as might be expected after the experiments with the cobalt glass.

Of the second group of curves, showing a displacement of the maximum towards the red, the one differing most and the one differing least from the writer's, are given in Fig. 11. An inspection of these curves shows the areas to be nearly the same as the area of the writer's curve, and neither curve differs from the writer's

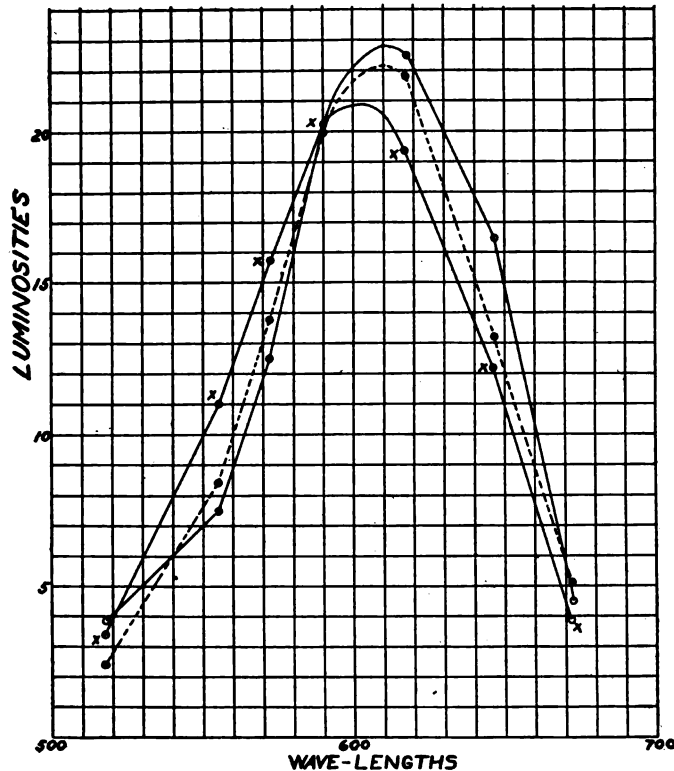


Fig. 11.

any more than the observer's curve in Fig. 8. Yet the observer of Fig. 8 showed no trace of color-blindness by the ordinary Holmgren test, while both of these observers were pronouncedly red-green color-blind.

While, therefore, the effect of light upon the color sense seems to be quite independent of its effect upon the luminosity sense, it would seem that an abnormal color sense is usually, if not always, associated with an abnormal wave-length luminosity curve. The

converse of this, however, is not true, and persons may be quite abnormal with respect to their color luminosity sense, and still be able to make perfectly normal judgments in sorting and matching colors.

It is well known that the peripheral portion of the retina is more sensitive to the luminous energy in the blue end of the spectrum than is the central portion (macula lutea), and the peripheral portion is known to contain a larger per cent. of rods than the central portion. If we assume that the wave-length luminosity curve for the rods is, with reference to the curve for the cones, displaced towards the blue end of the spectrum (and this seems the simplest explanation of these phenomena), then the differences in the positions of the maxima in the wave-length luminosity curves of different observers might be explained as due to differences in the ratio of rods to cones in the fovea centralis, if such a difference should be found to exist. Since it seems to be just as common for color-blind people to have wave-length luminosity curves displaced towards the red as towards the blue end of the spectrum, with reference to the normal curve, if the above explanation is accepted for the abnormal curves, it will not be possible to explain color-blindness as due to an abnormally large per cent. of rods in the fovea, as has sometimes been suggested (it being assumed that the cones alone contained the color sense organ).

While at present we have hardly sufficient data upon which to found a satisfactory theory of color vision, the above explanation of the differences in the luminosity of different colors (def. III.) as they appear to different observers seems to account very well for the phenomena described in this paper. Fatigue phenomena with color-blind eyes promise to give more definite information along these lines, and they are at present being investigated by the writer.

The form of flicker spectrophotometer here described lends itself readily to the determination of the per cent. of any spectrum color which must be mixed with a white of the same luminosity in order to be just discernible by the eye. Measurements which have been made upon normal eyes seem to give quite uniform results. Owing, however, to the difficulty of securing color-blind subjects who can give the requisite amount of time for the photometric tests, the collection of data is necessarily slow.

SUMMARY.

The results of the present investigation may be summed up as follows :

I. The retina of the human eye contains two distinct sense organs — one, the luminosity sense, the other, the color sense.

II. The luminosity sense is affected qualitatively in the same way by light stimuli of all wave-lengths within the visible spectrum so that it reacts, after fatigue, always in the same way, no matter what kind of light is used to fatigue the retina. (The only exception to this is when the fatigue is caused by prolonged exposure to the long, or red, rays of the spectrum.)

III. The relation between wave-length and luminosity (def. III.) in the case of a 50 C.P. incandescent lamp may be represented by a wave-length luminosity curve which, for most eyes, is identical with the curve in Fig. 6.

IV. Deviations from this normal curve fall, for the most part, into one or the other of two classes : (1) The point of maximum luminosity may be displaced towards the red, as in Fig. 8. (2) It may be displaced towards the green, as in Fig. 10.

V. Persons possessing perfectly normal color vision may have an abnormal wave-length luminosity curve, and color-blind persons as often have a wave-length luminosity curve belonging to class 1 as to class 2.

PHOENIX PHYSICAL LABORATORY,
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GENERAL LAW FOR VAPOR PRESSURES. PART II.

BY SANFORD A. MOSS.

IN the preceding article¹ was deduced a general law connecting saturation temperatures and vapor pressures for all substances, on the basis of a relation given by Ramsay and Young. The law connects the absolute saturation temperatures T_a and T_b of two substances, corresponding to the same vapor pressure, by the symmetrical relation

$$\frac{1}{T_b} = c \frac{1}{T_a} + k \quad (1)$$

c and k are constants for each pair of substances, for all vapor pressures. Either substance may be a vaporizing liquid or a subliming (volatilizing) solid. The two temperatures might also refer to the solid and liquid phases of the same substance.

Forms equivalent to (1) have also been derived from Ramsay and Young's relation by Ayrton and Perry² and J. D. Everett.³

As in the case of the original relation given by Ramsay and Young, we may determine by the law (1) the entire vapor pressure curve for a substance from two observations and the known curve of some standard substance.

In the preceding article the form (1) was supposed to be equivalent to the relation given by Ramsay and Young. However, it turns out that there are two quite different forms in which the statement of Ramsay and Young may be expressed mathematically. One form leads to the symmetrical law (1) and the other to a quite different non-symmetrical form. The latter form seems to be the one preferred by the authors of the original relation.

The purpose of this paper is to go into details in this matter, and

¹ PHYSICAL REVIEW, Vol. 16, 1903, p. 356.

² Phil. Mag., Vol. 21 (series 5), 1886, p. 259.

³ Phil. Mag., Vol. 4 (series 6), 1902, p. 335.

to show that the symmetrical law (1) is to be preferred over the other form for many reasons, and that it is very nearly, if not exactly, a law of nature. A number of related points discussed in various isolated papers will also be brought together systematically.

TEMPERATURE RATIO LAWS AND COMPARISON WITH OBSERVATIONS.

A relation exactly equivalent to (1) is

$$T_a/T_b = kT_a + c. \quad (2)$$

Hence we have the following as a consequence of the symmetrical law (1). If values of T_a/T_b , the ratio of absolute saturation temperatures at same vapor pressure for two substances, be found for various vapor pressures, and plotted against T_a , the *numerator* of the ratio, the points will lie on a straight line.

The fact that saturation temperature observations satisfied a law similar to the one just stated, was the particular point originally brought out by Ramsay and Young. At times they used the identical law above given, and at times another form, as will be discussed presently.

In this work, Ramsay and Young found that the constant k was always small so that the term kT_a is comparatively small as compared with c . Hence T_a/T_b is nearly but not quite constant. For the case of pairs of substances from a homologous series, such as the various ethers, k is zero, and the ratio T_a/T_b is exactly constant.¹

Now Ramsay and Young in some cases and Travers in all cases plot the absolute temperature ratio of (2) not against the *numerator*, but against the *denominator*. That is, they use the reciprocal of the left hand member of (2), corresponding to the dissimilar and non-symmetrical form

$$T_b/T_a = k'T_a + c'. \quad (3)$$

Evidently, if values of T_a/T_b give a straight line when plotted against values of T_a , so that (2) is satisfied, then values of the reciprocal, T_b/T_a , will not give a straight line but a curve. It will probably always be very flat, however, but nevertheless such that (3) is

¹Phil. Mag., Vol. 20, series 5, 1885, p. 530; Vol. 21, series 5, 1886, p. 33; Vol. 22, series 5, 1886, p. 37. Here the constant above called k is called c .

not exactly satisfied. If the values used are from observations and are slightly irregular, and if the range covered is not very great, the points may seem to follow a linear law, and may apparently satisfy the non-symmetrical form (3). It will be shown however that the points from various published observations fall in a straight line at least as well and often better, if the symmetrical form (2) is used rather than the non-symmetrical form (3) and also that it is more rational to use the symmetrical form.

In the original paper on the subject, by Ramsay and Young,¹ the law is given as being that the ratio of absolute saturation temperatures is a linear function of one of them. There is no statement as to which one, numerator or denominator. In the paper are given tables for the cases of ethyl alcohol, C_2H_6O , methyl alcohol, CH_4O , ethyl oxid, $C_4H_{10}O$, ethyl bromide, C_2H_5Br , ethyl chloride, C_2H_5Cl , ethylene, C_2H_4 , oxygen, O_2 (3 comparisons), and mercury, Hg, obtained by plotting actual vapor pressure observations according to the symmetrical form (2). That is, saturation temperature ratios are plotted against numerators. The law is shown to be verified as the observations lie very nearly on a straight line.

On the contrary, the opposite and non-symmetrical form (3) is used for a number of other substances and temperature ratio is plotted against denominator. No note is made regarding the change in procedure. Ayrton and Perry have made some remarks on this paper² and also seem to have noted the two different forms used. As already stated they deduce a form equivalent to (1) which they also regard as preferable on account of symmetry.

For the case of carbon bisulphid, CS_2 , one of the substances for which Ramsay and Young use the non-symmetrical form, the writer has replotted the given figures in the symmetrical form. The resulting points lie equally well on a straight line. A similar situation doubtless exists with the other cases where the non-symmetrical form was used, and the symmetrical form would undoubtedly have given at least as good results.

The paper gives as an algebraic expression of the law

$$R' = R + k(T' - T).$$

¹ Phil. Mag., Vol. 21, series 5, 1886, p. 33.

² Phil. Mag., Vol. 21, series 5, 1886, p. 259.

(The constant k is called c in the paper.) R and R' are ratios of absolute saturation temperatures of two substances at same vapor pressure, for two different vapor pressures. T and T' are temperatures of one of the substances. No statement is made as to which one, that of the numerator or denominator of the ratios. It is readily seen that this expression is equivalent to (2) or to (3) according as one or the other is used.

A similar expression is given by Ramsay and Travers in the classic paper, "Argon and its Companions,"¹ and is repeated on page 236 of Travers' "Study of Gases." This is printed in both places.

$$\frac{T_a}{T_b} = \frac{T'_a}{T'_b} + k(T_a - T'_a).$$

However, the writer has been informed by Professor Travers that this is a mistake and that the last parenthesis should have been $(T_b - T'_b)$, as is also indicated by the context. This correction calls for plotting of temperature ratio against denominator, contrary to the symmetrical form (2). In the paper on argon, and in "Study of Gases," examples are given of the application of the law and temperature ratios are always plotted against denominator. This may therefore be considered as the form of law preferred by Ramsay and Travers.

The preceding paper was based on the statement of the law given immediately above and the symmetrical form (2) deduced therefrom. The fact that the formula was not printed as the authors intended was not known to the writer at the time. The whole of the preceding paper goes to show that the symmetrical form (2) is correct, regardless of the fact that it was deduced from a misprint; and additional evidence is given in this paper.

In the paper, "Argon and its Companions," observed values of vapor pressure of krypton, argon and xenon are given, agreeing fairly well with the form (3). The writer has replotted these observations, using instead the form (2), and has found much better agreement. For the case of krypton two observations are not included in the range of the chart given by Ramsay and Travers, and these do not

¹ Phil. Trans., Vol. 197 A, 1901, p. 68.

lie on an extension of the line through the other points. However, when reciprocals of the ratio are used, corresponding to the form (2), these points, as well as all of the others, fall almost exactly on a straight line. In the case of argon, the form (2) fits slightly better than the other form, while in the case of xenon there is no material difference, owing to observational irregularities. Ramsay and Travers give tables of vapor pressures of argon, krypton and xenon, smoothed by the use of the form (3). Evidently the use of (2), the form preferred by the writer, would give slightly different tables.

The form (2) has been applied by the writer to Miller's observations of vapor pressure of SO_2 ¹, and found to agree very well for moderate temperatures, but to give some discrepancy at high values. The relation between T_s , the saturation temperature of SO_2 , and T_w , that of water vapor for the same pressure, is found to be

$$\frac{1}{T_s} = 1.6667 \frac{1}{T_w} - 0.00036.$$

In the preceding paper was given a table, reproduced herewith with some additions, for vapor pressures of water as computed from Ramsay and Young's observations on methyl alcohol by means of the law,

$$\frac{1}{T_w} = .9198 \frac{1}{T_a} - 0.0000307.$$

TABLE OF HIGH SATURATION TEMPERATURES OF WATER VAPOR.

Vapor Pressure. mm. Hg.	Saturation Temperatures, Degrees Centigrade.		
	From Methyl Alc. Obs.	From Cailletet's Obs.	From Formula "K."
45,000	275.9	274.8	276.0
50,000	282.9	281.5	283.0
55,000	289.3	288.0	289.5
60,000	295.2	294.0	295.6

Since the original table was published, observations by Cailletet have come to the attention of the writer, and interpolations from them are given in the table. They are very close to the computed figures, although slightly lower. It may be remarked however, that for lower pressures, Cailletet's temperature observations are slightly lower than those of both Regnault and Ramsay and Young,

¹ Trans. Amer. Soc. Mech. Engrs., Vol. 25, 1904, p. 182.

suggesting that all of his values may be slightly low. If so, the computed values are evidently almost exactly correct. The last column of the table will be referred to later.

INVESTIGATION OF RATIONALITY OF THE TEMPERATURE RATIO LAWS.

The law expressed by (1) is obviously mutual and $1/T_a$ and $1/T_b$ are each linear functions of the other. Similarly we may reverse (2) by writing it,

$$\frac{T_b}{T_a} = \left(-\frac{k}{c}\right)T_b + \frac{1}{c}.$$

Hence if we plot the reciprocal of the ratio on the left of (2) against the new numerator, we also have a linear relation. Hence if we use the form (2) it is immaterial as to which of a pair of substances is used as numerator or denominator. In other words the symmetrical form of the temperature ratio law is rational in so far that it is perfectly reversible.

The non-symmetrical form (3) does not turn out thus however. We may write it

$$\frac{T_a}{T_b} = \left(-\frac{k'}{c'}\right)\frac{T_a}{T_b} + \frac{1}{c'}.$$

Hence if T_b/T_a is a linear function of the denominator, T_a/T_b is not a linear function of the new denominator.

Hence if the form (3) is used for a given pair of substances, different results are obtained according to the one used as denominator and if the law holds in one form, the ratio cannot be inverted.

Another evidence of the rationality of the forms (1) and (2) is the fact that if the law holds for pairs consisting of two substances each compared with a third standard substance, it will necessarily hold for the pair consisting of the two different substances from the original pairs. Suppose for instance that the law holds for substances a and b and also for substances a and d . Then

$$\frac{1}{T_b} = c \frac{1}{T_a} + k,$$

$$\frac{1}{T_d} = c' \frac{1}{T_a} + k'.$$

All of the temperatures correspond to the same vapor pressure. By eliminating $1/T_a$ from the two equations we obtain

$$\frac{1}{T_b} = \left(\frac{c}{c'}\right) \frac{1}{T_a} + \left(k - k' \frac{c}{c'}\right).$$

Thus the linear relation holds for the pair of substances b and d .

On the contrary this does not occur with the form (3), and if two pairs of substances satisfy it, there is not satisfaction after interchange. Using the form (3) in the above case

$$\frac{T_a}{T_b} = kT_b + c.$$

$$\frac{T_a}{T_d} = k'T_d + c'.$$

Eliminating T_a by division,

$$\frac{T_d}{T_b} = \frac{kT_b + c}{k'T_d + c'}.$$

Hence the ratio T_d/T_b is not linear in the denominator T_b so that the law is not satisfied.

As already shown, the original relations of the case just investigated are not exactly reversible. Hence by using other arrangements of subscripts in them, we can obtain three more expressions for T_d/T_b all complicated and not giving the desired linear relation.

The point here discussed was originally mentioned by Findlay,¹ who showed it however by using relations only one of which was according to the non-symmetrical form (3), the other being according to the symmetrical form (2).

No doubt many sets of observed points would fit either of the forms fairly well on account of the flatness of the reciprocal curve for the short range usually covered, and the inevitable observational irregularities. However, the fact that the forms (1) or (2) permit of reversal and interchange makes them preferable if for no other reason.

Similar remarks apply to laws of the same form as (2) announced²

¹ *Zeit. phys. Chemie*, Vol. 42, 1902, p. 110.

² *Roy. Soc. Proc.*, Vol. 69, 1902, p. 471.

by Findlay for both chemical solubilities and equilibrium constants as functions of absolute temperature, instead of vapor pressures.

LATENT HEAT RATIO LAWS.

By differentiating (1) with respect to p , we obtain an expression which forms the basis of further relations

$$\frac{T_a^2 \frac{dp}{dT_a}}{T_b^2 \frac{dp}{dT_b}} = c.$$

For future purposes we write this

$$c \frac{\frac{1}{T_a} \frac{dT_a}{dp}}{\frac{1}{T_b} \frac{dT_b}{dp}} = \frac{T_a}{T_b}. \quad (4)$$

We also use the well-known thermodynamic relation for saturated vapor

$$\frac{u}{r} = \frac{1}{AT} \frac{dT}{dp},$$

where A is reciprocal of mechanical equivalent of heat, r is latent heat of vaporization, and u is difference between specific volumes of vapor and liquid. Except near the critical point, u approximates to the specific volume corresponding to saturation pressure and temperature, given by the perfect gas law and the molecular weight. By substituting from the last relation in (4)

$$c \frac{u_a/r_a}{u_b/r_b} = \frac{T_a}{T_b}, \quad (5)$$

From (2) it follows that

$$\frac{\frac{1}{T_a} \frac{dT_a}{dp}}{\frac{1}{T_b} \frac{dT_b}{dp}} = 1 + \frac{k}{c} T_a, \quad (6)$$

$$\frac{u_a/r_a}{u_b/r_b} = 1 + \frac{k}{c} T_a, \quad (7)$$

$$\frac{Ap u_a/r_a}{Ap u_b/r_b} = 1 + \frac{k}{c} T_a. \quad (8)$$

In other words, the ratio of either of the quantities $1/T \, dT/dp$, Apu/r or u/r , for two substances at the same vapor pressure has the same property as the ratio of absolute saturation temperatures, and is a linear function of the absolute temperature corresponding to the numerator. We remark that Apu/r is the ratio of external to total latent heat of vaporization, and that u/r is increase of volume per unit addition of latent heat. These laws, as in the case of the primary law, apply to subliming solids as well as to vaporizing liquids.

As stated, Ramsay and Young have shown that the constant k , and hence also k/c , is always very small, and is zero for homologous substances. Hence the quantities referred to are nearly alike for all substances at each vapor pressure, and exactly alike for homologous substances, as a consequence of the original law in the symmetrical form (1) or (2).

This was shown to hold for values of both Tdp/dT and r/u by actual computation of these quantities; and the essential features of the secondary law above referred to were given as independent empirical laws, by Ramsay and Young, prior to their announcement of the saturation temperature ratio law.¹ Referring to either of these quantities Ramsay and Young show that it is nearly the same for all substances at normal boiling point (saturation temperature corresponding to 760 mm. Hg vapor pressure) and that the ratio of values for any two given vapor pressures is nearly the same for all substances. These two relations are equivalent to the one given above, that values of $1/T \, dT/dp$, etc., are nearly the same for all substances at each vapor pressure.

Ramsay and Young also extended this approximate law to an exact form similar to (6)² giving it as an independent law however, and not as a consequence of the temperature ratio law, as here given. The evidence given by Ramsay and Young in support of the law is really evidence of the validity of the law (1) or (2).

In the paper alluded to, there are given tables from vapor pressure observations, of computed values of $T \, dp/dT$, and it is shown for a number of pairs of substances that the ratio $T_b \, dp/dT_b \div T_a \, dp/dT_a$ for

¹ Phil. Mag., Vol. 20, series 5, 1885, p. 515.

² Phil. Mag., Vol. 21, series 5, 1886, p. 136.

various vapor pressures, is a linear function of T_a . This is exactly the law given by (6). In this paper the law is given that the ratio is a linear function of one of the absolute temperatures, but it is not stated as to whether this is the one corresponding to the numerator or denominator of the ratio. However, in all of the examples given, the ratio is shown to be a linear function of the temperature corresponding to the denominator of the form used in the paper, that is, the numerator when the form is as in (6).

LATENT HEAT LAWS.

By means of (7) we may compute u_b/r_b for all vapor pressures for a substance b , from the value for any one vapor pressure, and values of u_a/r_a and T_a for some standard substance a such as water vapor. Then values of either r_b or u_b can be computed if the other is known. As already stated, u is the difference between specific volumes of liquid and vapor at the saturation point and r is the latent heat of vaporization. The law is probably exact although it may be only a close approximation.

A rough approximation of simpler form may be deduced from the preceding considerations. We may write (5) in the form

$$\frac{r_a}{r_b} = c \frac{T_b/u_b}{T_a/u_a}.$$

Now u differs from the specific volume in the gaseous state by the specific volume of the liquid, usually a small quantity. In most cases the gaseous volume is nearly that corresponding to the perfect gas laws, and is directly proportional to the absolute temperature and inversely proportional to the molecular weight. Hence T_a/u_a and T_b/u_b are practically proportional to the molecular weights since the pressure is the same for both substances. That is, we have approximately $r_a/r_b = \text{constant} = c \gamma_b/\gamma_a$. Here r_a and r_b are latent heats of vaporization for two substances at the same vapor pressure, and γ_a and γ_b are molecular weights. The latent heat ratio is constant for each pair of substances for all vapor pressures. This law will give a general idea of the latent heat of any substance for all pressures from any one value and from known values for the same pressures for some standard substance.

As a further approximation we may substitute from (2) in the last expression, neglecting k since it is always small. This gives

$$\frac{r_a}{r_b} = \frac{T_a}{T_b} \frac{\gamma_b}{\gamma_a},$$

or

$$\frac{r\gamma}{T} = \text{constant},$$

where γ is the molecular weight, or the "normal" density (at standard conditions, 760 mm. Hg and 0° C.), which is proportional to it; r is the latent heat of vaporization, and T is the corresponding saturation temperature. The constant is the same for all substances at a given vapor pressure. There is of course a different constant for each vapor pressure.

The approximate law thus rationally deduced was first given as an empirical law by Trouton,¹ being applied by him only for normal atmospheric pressure however. It is here extended to any pressure whatever.

EFFECT OF TEMPERATURE RATIO LAW ON GENERAL LAW FOR VAPOR PRESSURE.

A general relation between pressure and temperature of saturated vapor has long been sought without recognized success. No rational law holding from the supercooled region below the triple point up to the critical point, has ever been formulated. The temperature ratio law here discussed holds for this whole range however, so that it gives a condition which the general vapor pressure equation must satisfy almost if not quite exactly. This condition is that the vapor pressure p must be a function of $(A - B/T)$ where T is absolute saturation temperature and A and B are two constants, different for each substance.² Other constants if they occur, are the same for all substances. That is to say, we must have $p = f(A - B/T)$ or $\log p = f(A - B/T)$. This proposition is readily proven by noting that (1) may be written in the form

¹ Phil. Mag., Vol. 18 (series 5), 1881, p. 54.

² Ayrton and Perry, Phil. Mag., Vol. 21 (series 5), 1886, p. 259.

$$A_2 - \frac{B_2}{T_2} = A_1 - \frac{B_1}{T_1}.$$

Since the constant k is always small, A_1 and A_2 are nearly alike. Hence in the general expression $\log p = f(A - B/T)$ the constant A differs slightly for various substances and is exactly the same for homologous substances.

The mathematical form of statement that p is a function of $A - B/T$ is as follows: Let us first suppose that we are considering various homologous substances, for which A is constant. Then p and $A - B/T$ are each functions of the two independent variables B and T . Since by hypothesis p is also a function of $A - B/T$, we have from the mathematical "condition for functionality"

$$\left(\frac{dp}{dT}\right)_{AB} = -\frac{B}{T} \left(\frac{dp}{dB}\right)_{AT}.$$

In the same way, since A and T may be variable with constant B , we deduce the condition

$$\left(\frac{dp}{dT}\right)_{AB} = \frac{B}{T^2} \left(\frac{dp}{dA}\right)_{BT}.$$

A third equation can be formed, but it is not independent. The general vapor-pressure equation is the integral of these partial differential equations.

DIETERICI'S VAPOR PRESSURE LAWS.

Dieterici has proposed a vapor-pressure law equivalent to

$$7.4 p \frac{T_k dT}{T dp} = T$$

where T_k is the critical temperature. This gives as the relation between saturation temperatures T_a and T_b of two substances at the same vapor pressure

$$\frac{T_{ak}}{T_{bk}} \frac{\frac{1}{T_a} \frac{dT_a}{dp}}{\frac{1}{T_b} \frac{dT_b}{dp}} = \frac{T_a}{T_b}.$$

By comparison with (4), this law gives the value T_{ak}/T_{bk} for the constant c , so that (1) becomes

$$\frac{1}{T_b} = \frac{T_{ak}}{T_{bk}} \frac{1}{T_a} + k$$

or

$$\frac{1/T_b - k}{1/T_a} = \frac{T_{ak}}{T_{bk}}$$

where T_{ak} and T_{bk} are critical temperatures of the substances a and b .

If we plot reciprocals of absolute saturation temperatures corresponding to the same vapor pressure against each other, as is done in the chart of the previous article,¹ we obtain straight lines, as already shown. According to Dieterici's law the tangents of the angles of these lines with the horizontal will be proportional to the critical temperatures of the substances whose values of $1/T$ are plotted horizontally. Inspection of the chart shows that in a general way this is true, and that the less the angles the lower the critical temperatures. However, quantitative test of the law by measurement of the tangents of the angles of the vapor-pressure lines and comparison with observed critical temperatures shows that there is no approach to proportionality, and that the law is only a very roughly approximate one.

Dieterici's expression for vapor pressure when integrated gives a law of the form

$$\log p = A - \frac{B}{T}.$$

This is the simplest form of law agreeing with the conditions imposed by the temperature ratio law. However, as is well known, such a form does not at all represent observations, so that Dieterici's expressions are not exact.

VAPOR PRESSURE FORMULAS.

The temperature ratio law enables deduction of a law for vapor pressure of any substance from any of the empirical expressions for water-vapor pressure which can be put in the form $\log p = f(A - B/T)$. This was done in the preceding article for Rankine's law.² However this law does not give a very good representation of observations. On the contrary a law for pressure

¹ PHYS. REV., Vol. 16, p. 358.

² PHYS. REV., Vol. 16, p. 361.

of water vapör of a form suggested by Roche¹ but reconstructed and called by Regnault Formula K² gives excellent agreement with observations. The law is

$$p = aa^{\frac{T-253}{1+m(T-253)}}.$$

Regnault gives

$$\log a = 0.03833818 \quad \log a = 1.9590414 \quad m = 0.004788221.$$

This formula agrees very closely with the results of experiments by Regnault and Ramsay and Young³ and also with experiments at higher temperatures up to the critical point.⁴ In the preceding table of saturation temperatures of water vapor a column of values from this Formula K is given. They agree with values computed from methyl alcohol observations within a few tenths of a degree. In fact this formula agrees with any one series of observations as well as the various observers agree among themselves. It probably best represents our present experimental knowledge of water-vapor pressure from below triple point to the critical point.

This formula may be reduced to the general form consistent with the temperature ratio law, and then takes the form (exactly equivalent to the original form given above)

$$\log p = 45.8372 - (0.0264052 - 1.16589/T)^{-1}.$$

Here p is the pressure of water vapor in mm. Hg, and T is the corresponding absolute centigrade saturation temperature. For any other vapor we have as an expression which represents observations accurately

$$\log p = 45.8372 - (A - B/T)^{-1},$$

where A and B are constants for each substance. A is always close to 0.0264052 and has the same value for all substances of a homologous series. In both of these formulas the first constant becomes 44.1236 for pressure in lbs. per sq. in.

There is one class of proposed vapor-pressure formulas which

¹ Memoires de L'Institut, etc., Vol. 10, 1831, p. 227. As given by Roche, the formula does not agree at all with modern observations.

² Memoires de l'Institut, etc., Vol. 21, 1847, p. 613.

³ Phil. Trans., Vol. 183, 1892, p. 111.

⁴ Engineering, Vol. 83, January 4, 1907.

cannot be reduced to a form consistent with the temperature ratio law. These have the general form

$$\log p = A + B/T + C \log T.$$

This and similar relations have been deduced rationally by Rankine¹ and Gibbs² and others, but so far as the writer's knowledge extends, always for the region at a distance from the critical point, that is, for liquid volume small compared with vapor volume. This form is therefore not rational for the whole region from triple point to critical point. On the contrary the temperature ratio law applies to this whole region, so that concordance with the partial law above is not to be expected.

By empirically selecting the constants to suit, the above form may be applied to the whole region, and fair coincidence is found, since there are three arbitrary constants to choose. However, since this form is empirical and not rational when extended to the whole region, and since it gives no better representation of observations than the Roche law previously discussed, the Roche form is preferable since it is in accord with the temperature ratio law.

Comparison may be made of the temperature ratio law here discussed and the "law of corresponding states." Both laws give a relation between saturation temperatures for two substances, the former for the same vapor pressure, and the latter for vapor pressures bearing the same ratio to the critical pressures. The two laws are therefore distinct.

REDUCTION OF VAPOR PRESSURE OBSERVATIONS.

The form and exactness of the Roche law or "Formula K" suggests a modification of the method used in obtaining the charts of the previous article. We have for any vapor

$$A - B \frac{1}{T} = \frac{1}{45.8372 - \log p}$$

where p is vapor pressure in mm. Hg (constant is 44.1236 for lbs. per sq. in.), and T is the corresponding absolute centigrade saturation temperature. Hence if $1/T$ is plotted against $1/(45.8372 - \log p)$

¹ Phil. Mag., Vol. 31, series 4, 1866, p. 199.

² Scientific Papers (Thermodynamics), p. 152, footnote.

from observed values, the points should lie in a straight line, except for observational irregularities. The observations may be smoothed by readings from the straight line best representing the points, or by computation from the formula obtained by use of the numerical values of A and B obtained from the straight line.

The principle at the basis of this method is exactly the same as that used in obtaining the charts of the preceding article. Here however, the ordinates giving the vapor-pressures are obtained by formula instead of from tables of water vapor pressure.

ON THE DENSITY, ELECTRICAL CONDUCTIVITY
AND VISCOSITY OF FUSED SALTS AND
THEIR MIXTURES.

BY H. M. GOODWIN AND R. D. MAILEY.

Contributions from the Research Laboratory of Physical Chemistry No. 16.

THE present paper embodies the results of a research¹ carried out during 1905 and 1906, in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, its object being to obtain data on certain properties of fused salts with such a degree of precision that the following questions might be definitely settled or discussed :

1. The correct values of the specific and equivalent conductance of a number of fused salts which, from the discordance of published data, seemed in need of revision.
2. The temperature coefficient of both the specific and equivalent conductance of these salts.
3. The conductance of mixtures of fused salts with and without an ion in common.
4. The viscosity of pure fused salts and of their mixtures and its variation with the temperature.
5. The validity of Fousereau's Law of the proportionality between fluidity and electrical conductivity.
6. The ionization of fused salts.

During the progress of this investigation certain of the points considered have been made the subject of an independent investigation by Dr. H. T. Kalmus² in Professor Lorenz's laboratory in Zürich in which fortunately entirely different methods were employed both for conductivity and viscosity measurements. It is very gratifying

¹ This research was carried out under a grant from the Wm. E. Hale Research Fund, to the trustees of which grateful acknowledgment of the aid furnished by them is hereby made.

² *Zeit. für phys. Chem.*, 59, pp. 17, 244, 1907.

to find that the results of these two independent researches so far as they cover the same ground and permit of comparison are in essential agreement, which greatly increases the weight to be attached to each.

The literature on all matters even remotely bearing upon the question of the conductivity of fused electrolytes has been so exhaustively collected and admirably discussed by Professor Lorenz in his recently published monographs on the *Electrolyse Geschmolzener Salze* that a recompilation here is superfluous; everyone particularly interested in this branch of electrochemistry may be assumed to have a copy of Lorenz's work at hand. Reference will therefore be made to only those articles which are immediately related to our work.

The results of our research may conveniently be considered under the following subdivisions:

I. Discussion of matters common to all portions of the investigation such as construction of thermostats, measurement of temperature, purification of salts, etc.

II. Density determinations of the pure salts and of their mixtures over a wide range of temperature.

III. Conductivity measurements of the pure salts and of their mixtures over a corresponding range of temperature.

IV. Viscosity measurements of the same salts and mixtures over a corresponding range of temperature.

V. Summary.

I. GENERAL CONSIDERATIONS.

(a) *Thermostats. — Electric Furnaces.* — A preliminary precision discussion of the measurements to be undertaken made evident that the regulation, maintenance and measurement of the temperatures at which the conductivity and viscosity measurements were made was of fundamental importance, since the temperature coefficient of these properties of fused salts although less than the temperature coefficient of their corresponding aqueous solutions, is still large, in some cases over one per cent. per degree. There is no doubt that much of the discrepancy between the results obtained by previous investigators is due to inaccuracy in their temperature measurements. We therefore devoted considerable time to devising baths or thermostats in which temperatures up to 500° C. could be maintained

constant to a few tenths of a degree as long as desired, and to the measurement of these temperatures to the same degree of precision.

Three different types of thermostats or furnaces were therefore used in the progress of our work for maintaining the necessary temperatures for the density, conductivity, and viscosity measurements respectively.

The *first* was a vertical platinum resistance furnace of the usual type, the fire-clay cylinder on which the platinum was wound being 7.5 cm. in diameter and 25 cm. high, and packed in magnesium oxide. This furnace was used for heating the crucible containing the fused salt in the density measurements.

The *second* was an air-bath surrounded by a molten metal bath kept at constant temperature by electrical heating.

The *third* was a fused nitrate bath into which the viscosity apparatus was directly immersed.

The first of these furnaces needs no special description. The second contains some features worth mentioning and is shown in vertical section in Fig. 1.

The inner air bath *C*, in which the conductivity cell was suspended, was 32 cm. deep and elliptical in cross-section, the major and minor axes of the ellipse being about 8.5 and 2.5 centimeters respectively. This cross-section was chosen so as to reduce the air space about the conductivity cell to a minimum.

A deep bath was used in order that radiation from the top might not effect the temperature in the neighborhood of the conductivity cell. To further reduce the loss of heat to a minimum, the top of

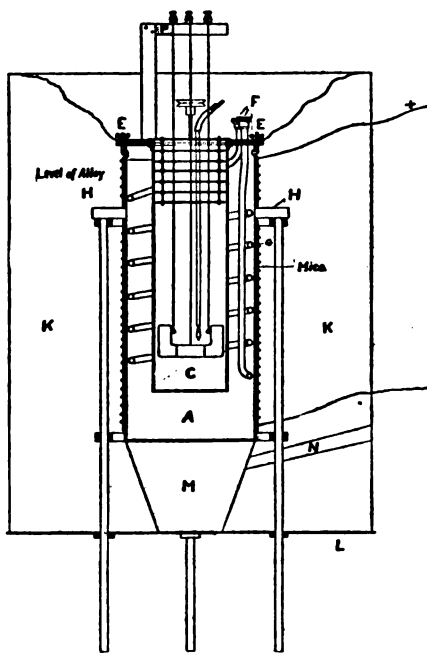


Fig. 1.

the air-bath was closed with a series of seven mica covers separated 1 cm. from one another. The necessary holes for the introduction of the thermo-electric junction and lead wires to the cell were cut through these covers which served not only to insulate but also to hold them in position in the furnace.

The inner cylinder *C* was fitted into a circular iron plate which formed the cover to the metal bath *A*. This cover was held in place by wing nuts *EE*. The iron pot *A* containing the metal was about 15.5 cm. in diameter and 38 cm. deep. It was filled to within 3 or 4 centimeters of the top with an alloy consisting of 30 per cent. lead and 70 per cent. tin, which melted at about 180° C. The molten mass was stirred by means of two screw propellers, not shown in the figures placed one on each side of the air-bath, *C*. These propellers were driven in opposite directions by an electric motor, and a thorough circulation of the bath was thus secured.

The furnace was heated by electricity. On the outside of *A* were wound 93 turns of No. 14 B. and S. nickel-steel wire, insulated from the iron by a layer of asbestos cloth and mica. This winding had a resistance of 22 ohms at room temperature and a resistance of about 28 ohms at 450° C. The current was regulated by an external rheostat; the energy absorbed was about 400 watts at 400° C. For lowering the temperature of the furnace, four meters of steel tubing, 7 mm. in diameter, were coiled about the inside wall of the pot. The ends *F* were brought out at the top of the furnace and one connected to the waste pipe, the other to a three-way cock by means of which air or water could be sent through the coil as desired. To reduce the violence of the vaporization within the tube when water was introduced, the outside of the tube was wound with a thin layer of asbestos. The primary object of this coil was to cool the bath rapidly when necessary, but it also proved very convenient in regulating the temperature.

For heat insulation an 11 cm. jacket *K* of asbestos fiber surrounded the whole apparatus, except the top. The fiber was held in place at the sides and bottom by asbestos paper. In the bottom an opening *M* was left with the chimney *N* so that the bath might be heated in part by a Bunsen burner when desired. The whole furnace was supported by lugs *H* which rested on an iron tripod.

The conductivity cell was suspended in the heater from a brass frame *P* mounted on the cover. At the top of this frame were three binding posts insulated from each other and from the furnace by hard rubber. From these posts the cell was suspended by platinum wires.

The temperature regulation in this furnace was effected by hand. When a desired temperature was reached the current was reduced by means of the rheostat until the heat supplied just balanced the radiation; the temperature could be held constant as long as desired to 0.2°C. up to 500° and over, by a slight variation of the current. Owing to the very large mass of the metal bath the fluctuations in temperature were very slow. If the temperature was found to be a little too high small quantities of air, blown through the cooling tube brought it back to the desired value. When it was necessary to cool the furnace any considerable amount, water was blown through the cooling tube. By this means the temperature could be reduced from 450°C. to 40°C. in 30 minutes, while by ordinary radiation the furnace cooled from 450°C. to only 100°C. in 15 hours.

The third thermostat used in connection with our viscosity investigation consisted of a bath of fused sodium and potassium nitrate. This was contained in an iron pot 23 cm. high and 15.5 cm. in diameter, the outside of which was wound with No. 14 B. and S. nickel-steel wire as in the type of furnace just described. The bath was heat insulated by asbestos fiber—twelve inches thick on the sides and seventeen inches on the bottom. An opening was left at the bottom so that the bath could also be heated by a Bunsen flame. This was used to keep the bath in a state of fusion, while the regulation of temperature was effected by the heating coil. Into this bath the viscosity apparatus was directly immersed.

(*b*) *Measurement of Temperature.*—All temperatures were measured by means of a carefully calibrated platinum-rhodium couple which gave about 8 microvolts per degree centigrade. The part of the couple inside the furnace was encased in a clay tube to within 3 or 4 centimeters of the junction. Outside the furnace the wires were covered by small rubber tubing. The cold junction, *i. e.*, where the copper leads joined the platinum and rhodium wires, was arranged as follows. Each soldered connection was pushed through

a small glass tube the lower end of which was then filled with sealing wax. These tubes were held in place in a test-tube by means of the cork stopper. The test-tube was filled with an insulating oil, and when measurements were in progress was packed in finely chopped ice in a 2-liter felt jacketed thermostat. By this means the cold junction was kept at a constant known temperature.

The thermo-electric force corresponding to any temperature of the hot junction was measured in a special slide wire potentiometer, in conjunction with a very sensitive low resistance d'Arsonval galvanometer as indicating instrument. The arrangement of apparatus is shown in Figs. 2 and 3. In Fig. 2 the slide-wire, a , is connected in

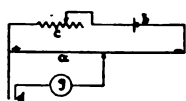


Fig. 2.

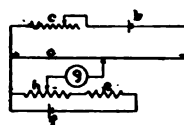


Fig. 3.

series with a storage cell, b , of large capacity, and c , a variable resistance; d is the couple, and g the galvanometer. When a balance point a_c , as indicated by no deflection of the galvanometer has been obtained, without changing the adjustment of a , b or c , the arrangement shown in Fig. 3 is thrown into the circuit in place of the thermal junction. Here e is a 20,000-ohm coil, h a variable resistance, and f a cadmium cell of special design. By adjusting h , a fraction of the voltage of the cadmium cell may be tapped off of such magnitude as will give a balance a_s on the slide-wire very near to the balance point obtained with the couple. From these readings the E.M.F. of the couple in terms of the E.M.F. of the standard cell may be calculated at once. If we let

e_c = E.M.F. of couple,

e_s = E.M.F. of standard cell,

a_c = reading on slide-wire with couple,

a_s = reading on slide-wire with standard,

R_h = resistance unplugged in h ,

R_e = 20,000 ohms,

R_f = internal resistance of standard cell,

the E.M.F. of the couple is given by the formula

$$e_c = e_s \frac{R_h}{R_s + R_h + R_s} \frac{a_c}{a_s}$$

In order that this calibration might be reliable a special form of standard cadmium¹ cell shown in Fig. 4 was used. The large electrode area gave a low internal resistance, about 20 ohms, and also prevented a change in E.M.F. due to polarization when the slight current was taken from it during a measurement. A low internal resistance was desirable on account of the variation in resistance with change in temperature (2.5 per cent. per 1° C.). To make sure that the E.M.F. of the cell remained constant, it was from time to time compared with a group of six Weston standard cells, in the standardizing laboratory.

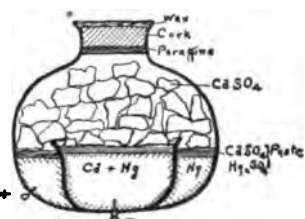


Fig. 4.

Thermo-electric disturbances in the various parts of the apparatus were eliminated by introducing the usual compensating device in the galvanometer circuit. A diagram of the complete arrangement of circuits as used in our measurements is given in Fig. 5.

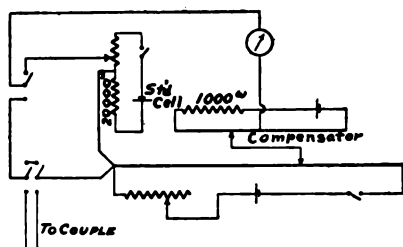


Fig. 5.

Calibration of Thermal Junction.

The thermo-electric couple was calibrated at four fixed points and from these data curves connecting temperature and electromotive force were plotted on a large scale (100 cm. square). The points taken were the boiling temperatures of water, naphthalene, benzophenone and sulphur. Distilled water was boiled in a steam-jacketed copper boiler such as is used for mercurial thermometer calibration, and the temperature of the steam calculated from the barometric pressure at time of observation.

¹ *Physiko-chemische Messungen* Ostwald-Luther, p. 361.

The naphthalene and benzophenone points were determined in upright boilers 50 cm. long by 5 cm. in diameter. The outside was covered with pipe covering, and concentric screens were placed inside to prevent radiation from the walls to the junction. The junction was suspended in the vapor space inside the screen, through a glass cover, glass being used in order that the level of the vapor could be observed and kept at the proper height in the boiler. A mica hood was placed just above the junction to prevent condensed vapor from running down on the couple. The temperature of the vapor was calculated from the barometric pressure at the time of measurement and the data given by Jacquerod and Wassmer,¹ on the boiling points of naphthalene and benzophenone.

For the sulphur point a boiler was used similar to that described above except that an additional screen was placed between the surface of the liquid sulphur and the junction, as recommended by Callender and Griffiths.² A mica hood was placed over the couple as in the other cases. The couple was suspended in the vapor to a depth of 22 cm. which was equal to the length introduced inside the furnace during the conductivity measurements.

The chemicals used for these vapor baths were from Kahlbaum. The naphthalene and benzophenone were recrystallized from alcohol. The sulphur was used as it came, since Callender and Griffiths used it in this way and we wished to reproduce the conditions of their experiments as nearly as possible and use the boiling point obtained by them.

The values which we used for our fixed joints are given below.

Substance.	Barometer.	Temperature.	dt/dp per mm.
Naphthalene	760 mm.	217.68 C.	0.058
Benzophenone	760	305.44	0.062
Sulphur	760	444.52	0.088

(c) *Preparations.*—In selecting salts for our investigation we required several whose melting point permitted them to be investigated over approximately the same range of temperature and which

¹Jour. de Chim. et de Phys., II., 52-78, 1904.

²Phil. Trans., 182 (A), pp. 119-158, 1891.

at the same time were univalent in order that the mutual effect of their dissociation might be as simple as possible. As the apparatus to be described was designed to give the precision desired only up to about 500° our choice was necessarily limited.

We chose, therefore, in the first instance, sodium and potassium nitrates, as fulfilling the above conditions, first, because existing data on these salts certainly needed revision and second, because the only existing viscosity measurements on fused salts (which we felt also needed confirmation) were on these two salts. To these we afterwards added lithium nitrate, silver nitrate, and silver chlorate, the last being chosen as a univalent salt of proper melting point which possessed no ion in common with the alkali nitrates.

These salts were, with the exception of silver chlorate, obtained from Baker & Co. and marked C.P. They were purified by repeated recrystallization until by the spectroscope practically all foreign metals were proved to be absent. They were then fused, cooled and ground to a powder and kept in a desiccator or glass stoppered bottle.

The silver chlorate was prepared by adding pure barium chlorate to a saturated solution of silver sulphate, filtering, and partially evaporating the filtrate. Upon cooling silver chlorate separated out in beautiful crystals. On account of the slight solubility of silver sulphate this process was somewhat tedious as many liters of filtrate had to be evaporated.

The mixtures were prepared by weighing out the calculated proportions of the two component salts (these having been previously fused), fusing the two together, cooling, and regrinding the mass in a mortar to a fine power.

Freezing Point of the Salts and their Mixtures.

Although data on the melting or freezing point of most of the salts which we investigated are given in Landolt & Börnstein's tables, we determined the value for our preparations, as this involved little extra work and served to indicate the purity of the salts.

For each determination not less than 15 c.c. of fused salt was used; this was contained in a platinum crucible, placed in the platinum resistance furnace. The melt, which was continuously stirred,

was allowed to cool slowly, and the temperature at which the rate of cooling became zero was taken as the freezing point.

All temperatures were determined with the thermo-electric junction. In the case of the mixtures small crystals of the solid mixture were dropped into melt to prevent under-cooling. The values given in the following table are the mean of several determinations together with their average deviations. Our values for alkali nitrates are about three degrees lower than those obtained by Carveth using a mercury thermometer, an amount greater than the deviations among the measurements themselves. On the other hand, our values on the mixtures of sodium and potassium nitrates agree very well with the values found by him.

Freezing Point Data.

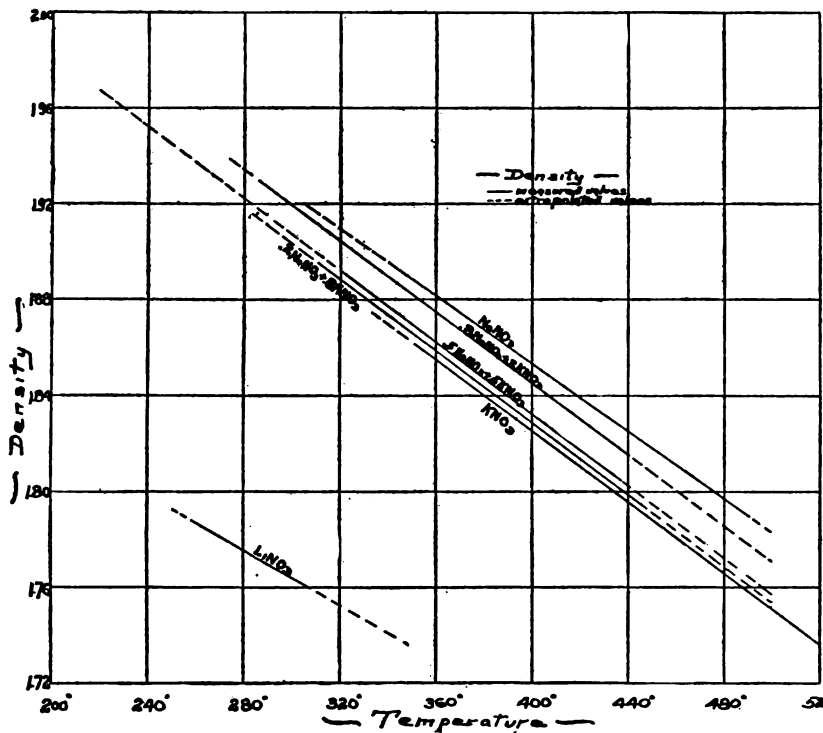
Salt.	G. and M.	Carnelley.	Carveth.
KNO ₃	333.7 ± 0.0	339.0	337
NaNO ₃	305.6 ± 0.4	319.0	308
LiNO ₃	250.2 ± 0.5	264	253
AgClO ₃	215.0 ± 1.5	—	—
AgNO ₃	218.0 ± 1.0	217 ± 2	—
0.2 KNO ₃ + 0.8 NaNO ₃	274 ± 2	—	273
0.5 KNO ₃ + 0.5 NaNO ₃	220 ± 0.5	—	221
0.8 KNO ₃ + 0.2 NaNO ₃	284.0 ± 1.5	—	285

II. MEASUREMENT OF DENSITY.

The density determinations were made with a modified form of Westphal balance, in which the sinker used was constructed of fused silica for densities less than 2.6, and with a delicate analytical balance from one pan of which a platinum ball was suspended, for greater densities. Fused silica is admirably adapted for a sinker, since its change of volume over wide ranges of temperature is very slight and easily calculated from its known coefficient of expansion. Moreover, its density being low, it is very sensitive to changes in the density of the liquids in which it is suspended. The volume of the silica sinker which we used was about 11 c.c., that of the platinum ball 9 c.c. In constructing the set of Westphal weights the following method was used. The balance was adjusted for equilibrium with the sinker freely suspended at the end of the

balance arm. The sinker was then suspended in distilled water at 4° C. and its loss in weight accurately determined. A set of decimal weights of the usual Westphal form was then constructed with this weight as a unit. With such a series of weights, densities up to 2.6 could be measured to the third place of decimals, while the fourth place could be estimated by observing the swing of the balance. The only correction to be applied to the observed densities was for the expansion of the sinker for which $\alpha = 0.0000021$ ¹ for vitreous quartz; for the platinum ball $\alpha = 0.00002668$.²

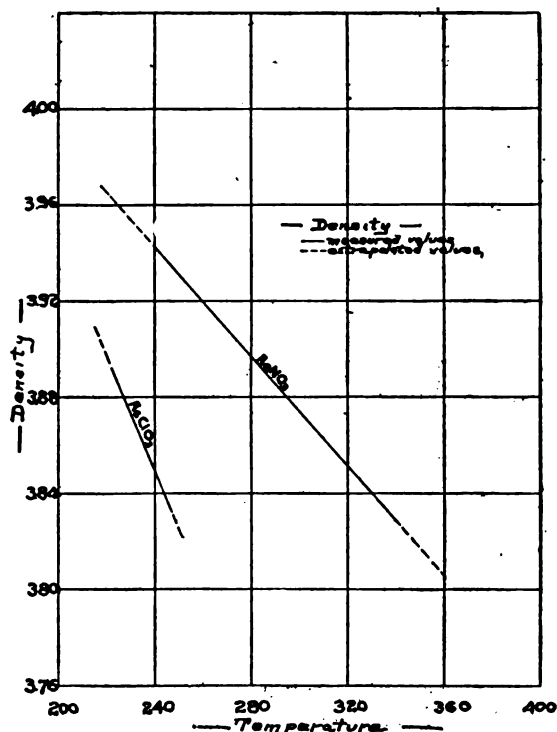
In measuring the densities of the fused salts, the balance was placed upon a table over the platinum resistance furnace so that the sinker, suspended by fine platinum wire, hung in a cylindrical platinum crucible placed inside the furnace. This crucible



Plot I.

¹C. R., 130, p. 1703, 1900.²Ann. der Physik, 2, p. 509, 1900.

contained the salt whose density was to be determined. The temperature was measured with a thermo-couple, the junction being placed in the fused salt along with, but not touching, the sinker. By varying the temperature of the furnace, rapid and accurate measurements of the density of the fused salts could be made at different temperatures with ease. Independent determinations agreed well within 0.1 per cent.

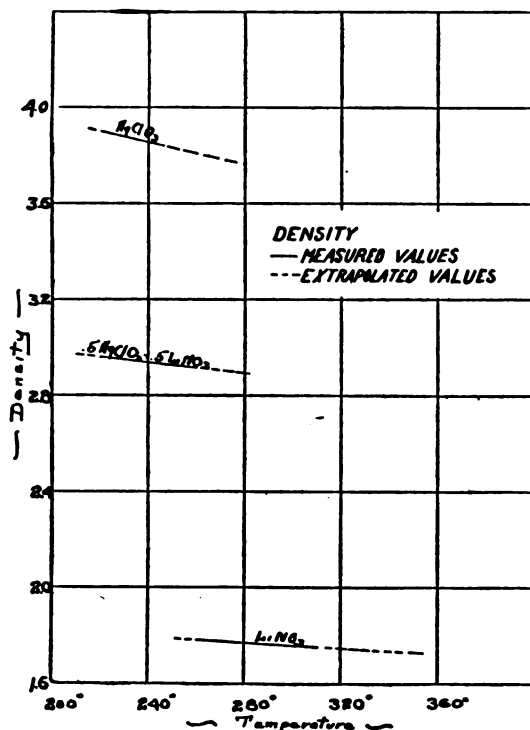


Plot II.

The observed data on the pure salts are given in Tables I. to V. and those on the mixtures in Tables VI. to IX. respectively. These data were plotted, the best representative line for each salt or salt mixture found, and its equation determined. The density-curves are shown on a reduced scale in Plots I., II. and III. The dotted portion of a line represents an extrapolation beyond the actual observations. The equations expressing the density as a function

of the temperature are in all cases linear over the range of temperature studied, the agreement between the observed values and values computed from these formulæ being better than 0.1 per cent.

In Tables Ia to IXa are given the values of the density for each salt and salt mixture at intervals of ten degrees, the values being interpolated directly from the original plots. The corresponding values of the specific volume, $S = 1/D$, are given in column three.



Plot III.

The values of the molecular volume $\phi = MS$ have also been computed for the pure salts and are given in column four, Tables Ia to Va.

Tables VIa to IXa contain in addition to values of the density and specific volume of the several mixtures the values of the specific volume of the mixture computed from the respective specific volumes of the components. The values below 350° are calculated

from the densities which the pure salts would have if they could be cooled to the temperatures in question without solidifying. These were computed from the formulae given below, Tables I. and II. respectively. The computed specific volumes are given in column four, and the differences between observed and computed values are given in column five. It will be seen that in every case, except the last (Table IXa), mixture of the salts is accompanied by a slight

TABLE I.

Density of NaNO_3 Referred to H_2O at 4°C .

Temperature.	Density Observed.	Density Computed.	Difference.
342.6	1.893	1.893	$\pm .000$
400.8	1.852	1.852	$\pm .000$
433.6	1.828	1.829	$+.001$
452.4	1.814	1.814	$\pm .000$
491.5	1.789	1.789	$\pm .000$

$$D_t = 1.853 [1 - 0.000379 (t - 400)].$$

TABLE Ia.

Specific and Molecular Volume of NaNO_3 . Molecular Weight: $M = 85.09$.

Temperature.	Density. D .	Specific Volume. S .	Molecular Volume. $\phi = MS$.
305 M.P.	1.920	0.5208	44.32
320	1.909	0.5240	44.57
330	1.902	0.5258	44.74
340	1.895	0.5278	44.90
350	1.888	0.5299	45.07
360	1.880	0.5319	45.26
370	1.873	0.5340	45.43
380	1.866	0.5361	45.60
390	1.859	0.5382	45.77
400	1.852	0.5400	45.95
410	1.845	0.5417	46.12
420	1.838	0.5444	46.29
430	1.831	0.5461	46.47
440	1.824	0.5481	46.65
450	1.817	0.5500	46.83
460	1.810	0.5525	47.01
470	1.803	0.5545	47.19
480	1.796	0.5566	47.38
490	1.789	0.5586	47.56
500	1.782	0.5611	47.75

TABLE II.

Density of KNO₃ Referred to H₂O at 4° C.

Temperature.	Density Observed.	Density Computed.	Difference.
352.0	1.858	1.861	+ .003
365.0	1.853	1.852	— .001
372.3	1.847	1.846	— .001
391.5	1.832	1.832	± .000
404.6	1.823	1.823	± .000
421.4	1.809	1.810	+ .001
427.8	1.804	1.805	+ .001
443.9	1.794	1.794	± .000
451.0	1.785	1.788	+ .003
468.0	1.775	1.776	+ .001
497.0	1.756	1.754	— .002
504.0	1.749	1.749	± .000
535.0	1.726	1.726	± .000
553.9	1.712	1.712	± .000
554.0	1.714	1.712	— .002
564.0	1.706	1.705	— .001

$$D_t = 1.826 [1 - 0.000405 (t - 400)].$$

TABLE IIa.

Specific and Molecular Volume of KNO₃. Molecular Weight: M = 101.18.

Temperature.	Density. <i>D.</i>	Specific Volume. <i>S.</i>	Molecular Volume. $\phi = MS.$
333.7 M.P.	1.875	0.5335	53.96
340	1.870	0.5348	54.11
350	1.863	0.5368	54.31
360	1.856	0.5390	54.51
370	1.848	0.5407	54.75
380	1.841	0.5431	54.96
390	1.833	0.5456	55.20
400	1.826	0.5474	55.41
410	1.818	0.5497	55.66
420	1.811	0.5521	55.87
430	1.804	0.5542	56.08
440	1.796	0.5566	56.34
450	1.789	0.5586	56.56
460	1.782	0.5611	56.78
470	1.774	0.5636	57.05
480	1.767	0.5657	57.39
490	1.759	0.5682	57.52
500	1.752	0.5707	57.75
510	1.745	0.5729	57.98

TABLE III.

Density of LiNO₃ Referred to H₂O at 4° C.

Temperature.	Density Observed.	Density Computed.	Difference.
259.9	1.788	1.788	±.000
267.3	1.785	1.783	— .002
269.9	1.782	1.782	±.000
281.3	1.775	1.775	±.000
281.5	1.775	1.775	— .001
297.0	1.766	1.766	±.000
308.8	1.760	1.760	±.000

$$D_t^* = 1.776 [1 - 0.000322 (t - 280)].$$

TABLE IIIa.

Specific and Molecular Volume of LiNO₃. Molecular Weight: M = 69.07.

Temperature.	Density. <i>D.</i>	Specific Volume. <i>S.</i>	Molecular Volume. $\phi = MS.$
250 M.P.	1.794	0.5573	38.50
260	1.788	0.5590	38.63
270	1.782	0.5611	38.76
280	1.776	0.5629	38.89
290	1.771	0.5646	39.00
300	1.765	0.5664	39.13
310	1.759	0.5682	39.27
320	1.753	0.5703	39.40
330	1.747	0.5722	39.54
340	1.742	0.5741	39.65
350	1.736	0.5760	39.79

TABLE IV.

Density of AgNO₃ Referred to H₂O at 4° C.

Temperature.	Density Observed.	Density Computed.	Difference.
239.0	3.944	3.941	— .003
244.5	3.935	3.935	±.000
254.0	3.926	3.924	— .002
262.0	3.913	3.915	+ .002
306.5	3.864	3.866	+ .002
309.0	3.864	3.863	— .001
342.0	3.829	3.826	— .003

$$D_t = 3.8734 [1 - 0.000287 (t - 300)].$$

TABLE IVa.

Specific and Molecular Volume of AgNO₃. Molecular Weight: M=169.97.

Temperature.	Density. <i>D</i> .	Specific Volume. <i>S</i> .	Molecular Volume. $\phi = MS$.
218 M.P.	3.964	0.2522	42.88
230	3.952	0.2531	43.01
240	3.940	0.2538	43.14
250	3.929	0.2545	43.26
260	3.918	0.2552	43.38
270	3.907	0.2559	43.50
280	3.896	0.2567	43.63
290	3.885	0.2573	43.75
300	3.873	0.2582	43.89
310	3.863	0.2589	44.00
320	3.851	0.2596	44.14
330	3.840	0.2604	44.26
340	3.829	0.2612	44.39
350	3.818	0.2619	44.52
360	3.807	0.2627	44.69

TABLE V.

Density AgClO₃ Referred to H₂O at 4°C.

Temperature.	Density Observed.	Density Computed.	Difference.
223.0	3.872	3.874	+ .002
230.3	3.861	3.861	± .000
231.5	3.859	3.859	± .000
247.0	3.831	3.832	+ .001

$$D_t = 3.8619 [1 - 0.000451 (t - 230)].$$

TABLE Va.

Specific and Molecular Volumes of AgClO₃. Molecular Weight: M=191.37.

Temperature.	Density. <i>D</i> .	Specific Volume. <i>S</i> .	Molecular Volume. $\phi = MS$.
200	3.934	0.2452	48.65
210	3.897	0.2566	49.11
215 M.P.	3.888	0.2572	49.22
220	3.879	0.2578	49.33
230	3.862	0.2589	49.55
240	3.844	0.2601	49.78
250	3.827	0.2613	50.00

expansion, *i. e.*, the observed specific volume is greater than that which the mixture would possess did no change in the volume of the components occur on mixing. Although this difference is small, it is unmistakable, being greater than the limits of experi-

TABLE VI.

Density of Mixture of 2 Mols KNO_3 + 8 Mols $NaNO_3$ Referred to H_2O at $4^\circ C$.

Temperature.	Density Observed.	Density Computed.	Difference.
286.2	1.927	1.928	+ .001
332.4	1.894	1.894	$\pm$.000
363.4	1.870	1.870	$\pm$.000
412.0	1.835	1.835	$\pm$.000
440.8	1.816	1.814	— .002

$$D_t = 1.844 [1 - 0.000400 (t - 400)].$$

TABLE VIa.

Specific Volume of 2 Mols KNO_3 + 8 Mols $NaNO_3$.

Temperature.	Density. <i>D.</i>	Specific Volume. <i>S.</i>	Specific Volume Computed.	Difference.
274 M.P.	1.937	0.5163	0.5162	0.0001
290	1.925	0.5195	0.5194	0.0001
300	1.918	0.5214	0.5213	0.0001
310	1.910	0.5236	0.5232	0.0004
320	1.903	0.5255	0.5252	0.0003
330	1.896	0.5274	0.5271	0.0003
340	1.888	0.5297	0.5292	0.0005
350	1.881	0.5317	0.5313	0.0004
360	1.874	0.5336	0.5333	0.0003
370	1.866	0.5359	0.5353	0.0006
380	1.859	0.5379	0.5375	0.0004
390	1.852	0.5400	0.5397	0.0003
400	1.844	0.5423	0.5415	0.0008
410	1.837	0.5443	0.5433	0.0010
420	1.830	0.5464	0.5459	0.0005
430	1.823	0.5485	0.5477	0.0008
440	1.815	0.5509	0.5498	0.0011
450	1.808	0.5532	0.5517	0.0015
460	1.801	0.5552	0.5542	0.0010
470	1.793	0.5576	0.5563	0.0013
480	1.786	0.5591	0.5584	0.0007
490	1.779	0.5618	0.5605	0.0013
500	1.771	0.5645	0.5630	0.0015

mental error. Inspection of the column of differences in the tables further shows :

1. The difference between observed and computed values tends to increase slightly with rising temperature.

2. The difference resulting from mixing 2 mols KNO_3 with 8 mols NaNO_3 is less, than that resulting from mixing 2 mols NaNO_3 with 8 mols KNO_3 .

TABLE VII.

Density of Mixture of 5 Mols KNO_3 + 5 Mols NaNO_3 Referred to H_2O at 4°C .

Temperature.	Density Observed.	Density Computed.	Difference.
320.8	1.891	1.891	$\pm .000$
365.0	1.858	1.858	$\pm .000$
414.5	1.821	1.821	$\pm .000$
437.0	1.804	1.804	$\pm .000$

$$D_t = 1.832 [1 - 0.000408 (t - 400)].$$

TABLE VIIa.

Specific Volume of 5 Mols KNO_3 + 5 Mols NaNO_3 .

Temperature.	Density. <i>D.</i>	Specific Volume. <i>S.</i>	Specific Volume Computed.	Difference.
220 M.P.	1.967	0.5084	0.5078	0.0006
300	1.907	0.5245	0.5232	0.0007
310	1.899	0.5268	0.5251	0.0017
320	1.892	0.5286	0.5272	0.0014
330	1.884	0.5309	0.5291	0.0018
340	1.876	0.5333	0.5313	0.0020
350	1.869	0.5353	0.5334	0.0019
360	1.862	0.5371	0.5355	0.0016
370	1.854	0.5395	0.5374	0.0021
380	1.847	0.5410	0.5396	0.0014
390	1.839	0.5441	0.5419	0.0022
400	1.832	0.5459	0.5437	0.0022
410	1.824	0.5481	0.5457	0.0024
420	1.817	0.5500	0.5483	0.0017
430	1.809	0.5524	0.5502	0.0022
440	1.802	0.5549	0.5524	0.0025
450	1.794	0.5573	0.5543	0.0030
460	1.786	0.5597	0.5568	0.0029
470	1.779	0.5618	0.5591	0.0027
480	1.771	0.5646	0.5612	0.0034
490	1.764	0.5668	0.5634	0.0034
500	1.757	0.5689	0.5659	0.0030

3. The difference is a maximum for equimolecular mixtures of these two salts, becoming for this mixture as great as 0.5 per cent.

4. The specific volume of sodium and of potassium nitrates in mixtures of the two salts at temperatures below those at which the pure salts can exist in the liquid state, can be calculated by a linear extrapolation of their respective densities below their melting point.

5. Mixtures of silver chlorate and lithium nitrate show a decided

TABLE VIII.

Density of Mixture of 8 Mols KNO_3 + 2 Mols $NaNO_3$ Referred to H_2O at $4^\circ C$.

Temperature.	Density Observed.	Density Computed.	Difference.
312.6	1.894	1.893	— .001
383.6	1.840	1.840	$\pm .000$
445.8	1.793	1.793	$\pm .000$

$$D_t = 1.828 [1 - 0.000407 (t - 400)].$$

TABLE VIIIa.

Specific Volume of 8 Mols KNO_3 + 2 Mols $NaNO_3$.

Temperature.	Density. <i>D.</i>	Specific Volume. <i>S.</i>	Specified Volume Computed.	Difference.
284 M.P.	1.914	0.5226	0.5218	0.0008
300	1.902	0.5258	0.5251	0.0007
310	1.896	0.5276	0.5270	0.0006
320	1.889	0.5296	0.5292	0.0004
330	1.881	0.5316	0.5311	0.0005
340	1.873	0.5340	0.5334	0.0006
350	1.866	0.5361	0.5354	0.0007
360	1.858	0.5385	0.5375	0.0010
370	1.851	0.5402	0.5394	0.0008
380	1.843	0.5424	0.5417	0.0007
390	1.835	0.5451	0.5441	0.0010
400	1.828	0.5467	0.5459	0.0008
410	1.820	0.5495	0.5481	0.0014
420	1.812	0.5518	0.5505	0.0013
430	1.805	0.5538	0.5526	0.0012
440	1.797	0.5562	0.5549	0.0013
450	1.790	0.5587	0.5569	0.0018
460	1.782	0.5611	0.5594	0.0017
470	1.774	0.5636	0.5618	0.0018
480	1.767	0.5657	0.5639	0.0018
490	1.759	0.5682	0.5663	0.0019
500	1.752	0.5707	0.5688	0.0019

contraction in volume upon mixing, the contraction amounting in the case of equimolecular quantities to 1.6 per cent. In this case it is to be noted that the two components contain no common ion as in the preceding mixtures of sodium and potassium nitrate.

TABLE IX.

Density of Mixture of 5 Mols AgClO_3 + 5 Mols LiNO_3 Referred to H_2O at 4°C .

Temperature.	Density Observed.	Density Computed.	Difference.
223.5	2.953	2.953	$\pm .000$
230.7	2.946	2.946	$\pm .000$
244.1	2.930	2.931	$+ .001$
251.1	2.925	2.924	$- .001$
259.8	2.914	2.914	$\pm .000$

$$D_t = 2.936 [1 - 0.000366 (t - 240)].$$

TABLE IXa.

Specific Volume of 5 Mols AgClO_3 + 5 Mols LiNO_3 .

Temperature.	Density. <i>D.</i>	Specific Volume. <i>S.</i>	Specific Volume Computed.	Difference.
210	2.968	0.3369	0.4037	-0.0668
220	2.957	0.3382	0.4052	-0.0670
230	2.946	0.3394	0.4065	-0.0671
240	2.936	0.3406	0.4080	-0.0674
250	2.925	0.3419	0.4095	-0.0676

The values of the specific and molecular volumes given in the above tables will be made use of in the computation of the molecular conductance and fluidity of the salts, which properties will be considered in the following divisions of this paper.

(To be continued.)

THE VAPOR PRESSURE OF CARBONIC ACID.

BY JOHN ZELENY.

IN the May number of the *PHYSICAL REVIEW* Professor du Bois calls attention to a possible difference in the cryogenic properties of the snow obtained from commercial carbonic acid of different manufacture. He states that in their experiments for getting the vapor pressure of solid carbonic acid, he and Wills¹ used commercial gas which had been made from coke and contained at least 99.5 per cent. of carbonic acid with possible traces of air, water and grease.

As the results of some similar determinations made in this laboratory were published in this journal,² I wish to make some additional statements about the nature of the gas used. In the first place the gas coming from the cylinder was found to be perfectly odorless. In the experiments performed by Smith and me for determining the vapor pressure of liquid and solid carbonic acid at low temperatures, the gas was freed from its admixed air by allowing it to flow into a glass tube, the lower end of which was immersed in liquid air. The carbonic acid gradually froze at the bottom of this tube, while the air escaped. The gas obtained from this solid carbonic acid was almost completely absorbed by KOH, the residue being approximately one fortieth of one per cent.

I have since written to the company which supplied the gas, and they inform me that the gas was collected from fermenting vats and then passed in succession through four purifiers, each twenty feet high, the materials of which were copiously sprayed with water. The gas was then passed through calcium chloride on the way to the compressor. They inform me, further, that as shown by daily tests made at the factory, the gas obtained by this process is exceptionally pure, containing only a small amount of air and no traces of any vegetable substances.

¹ du Bois and Wills, *Verh. der D. Phys. Gesell.*, I., p. 168.

² J. Zeleny and R. H. Smith, *PHYS. REV.*, 24, p. 42; J. Zeleny and A. Zeleny, *PHYS. REV.*, 23, p. 308.

It would thus appear that the gas we used was of good purity. The effect of any impurity upon the vapor pressure of a solid is somewhat uncertain, depending not only upon its nature but also upon whether it is just mechanically mixed with the substance or whether it forms a solid solution with it.

The experiments which I carried out with A. Zeleny show that neither alcohol nor ether added to carbonic acid snow so as to form a thick mush with it, affects its vapor pressure appreciably over a wide range of temperatures. The temperature-vapor pressure curve obtained with these mixtures, the temperature at any pressure being acquired by the evaporation of the carbonic acid, was found to agree well with the curve obtained by Smith and me where the pure solid carbonic acid was maintained at different temperatures by the aid of liquid air.

We used the temperature of a mixture of alcohol and carbonic acid as determined by Holborn,¹ in Berlin, with a hydrogen thermometer as one of the calibration points for our thermo-element, and the point on the calibration curve was in harmony with the other points used. The results obtained with our carbonic acid for the vapor pressure of the liquid up to 25 atmospheres pressure and for the solid for pressures above one atmosphere agree well with the results obtained by Kuenen and Robson² in Scotland. Such agreements point to the absence of deleterious impurities.

I agree with Professor du Bois that it is difficult to get the value of $dP/d\theta$ accurately at 76 cm. pressure from the experimental curves. The value of the tangent being in the neighborhood of 6, a change of 1° in the inclination of the curve at the desired place makes a change of about 10 per cent. in the tangent. Still, the error in drawing the curve with its true inclination is apt to be less where the experimental points extend a considerable distance to each side of the 76 cm. as they did in the case of Smith and myself, than where they end close to the 76 cm. point.

THE PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
July 20, 1907.

¹ Holborn, *Annal. der Physik*, 6, p. 245.

² Kuenen and Robson, *Phil. Mag.* (6), 3, p. 149.

A TRANSPORTABLE FORM OF STANDARD CELL.

BY RALPH E. DELURY.

THE ordinary or H-form of cell and also its modification, the Λ -form, possess the disadvantage that they are not transportable. Rough handling will cause the contents of the two legs to mix thus destroying the cell as a standard. In the cell described below, the contents cannot mix even though the cell be inverted or shaken. A glance at Fig. 2 will show the shape of the cell. It may be made as follows:

Take a piece of tubing *A*, Fig. 1, of suitable thickness, 15 or 20 cm. long and 1.5 to 2.5 cm. in diameter. Take another piece *B*,

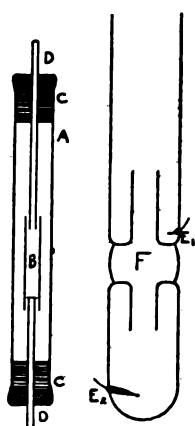


Fig. 1. Fig. 2.

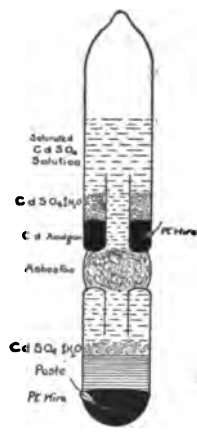


Fig. 3.

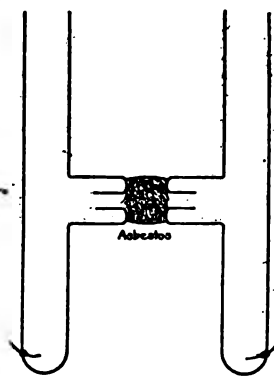


Fig. 4.

6 to 8 cm. long and 0.5 to 1.0 cm. in diameter. Place *B* inside *A* and insert in the ends of *A* tight-fitting corks *C* through which pass the small tubes *D* one of which is open, the other sealed. Adjust the lengths of the tubes *D* so that they enter *B* just enough to hold it co-axial with *A*. The whole is held horizontally and is rotated in the small pointed flame of a blowpipe — or better in the flames of two blowpipes pointing into one another. The tube *A* is melted

in a narrow band nearly opposite the middle of *B*. At this point *A* adheres to *B* and after the tubes are thoroughly fused together they are blown out. While the tube is still warm the platinum wire E_1 is fused in above the bulb of the cell, in the usual manner. The corks are now withdrawn and one end of the cell is sealed and another platinum wire E_2 fused into it. With a little practice the cell can be constructed in less time than it takes to make an H-form of cell.

The cell now appears as in Fig. 2. If it is to be used in a water thermostat, it may be placed in a test-tube containing an oil such as kerosene, to prevent short-circuiting; or the wire E_1 may be replaced by another sealed into a small tube which may pass through a cork above or may be sealed into the cell 5 or 6 cm. above the bulb *F* and pass down inside to a point just above *F*.

The cell is filled as follows :

Put mercury in the bottom of the tube by means of a small pipette or funnel made by drawing out a test-tube. Above this place the mercurous sulphate paste and cadmium sulphate crystals by means of a small tube. Then by means of a pipette put into the cell sufficient saturated cadmium sulphate solution to fill the bulb *F*. Air will thus be entrapped below *F*, and to remove it apply suction at the end of the cell. On removing the suction the solution will rush down to fill the space below the bulb. Now press some asbestos or glass-wool down through the inside tube to fill the bulb *F*, packing it in fairly tightly, yet not so compactly as to make the internal resistance of the cell too great. Then put enough cadmium amalgam in the space above *F* to cover the platinum wire E_1 completely. Above this place cadmium sulphate crystals and add enough saturated cadmium sulphate solution to fill the cell about a centimeter above the end of the inside tube. Several centimeters above this, seal up the tube or insert a cork and the cell is completed as represented in Fig. 3. The Clark cell may of course be set up in the same way.

It is impossible to mix the contents of the anode and cathode compartments. If the cell is turned over the mercury runs down and is caught below the bulb, and when the tube is placed erect again the mercury returns to its original position. The amalgam, if

it moves at all, will behave in a similar manner. If any mercury or amalgam or mercurous sulphate falls into either end of the inside tube, the asbestos in the bulb will prevent it from going into the other compartment.

The H-form of cell is made transportable by employing a similar "double-trap" in the cross-tube connecting the two legs, as shown in Fig. 4. In this case the asbestos should be put into the bulb before the cross-tube is sealed to the legs.

Some cells like the above were made during the past year in the laboratory of physical chemistry, Princeton University, while working under the direction of Dr. Hulett on the subject of standard cells, in fact this cell is a modification of a form suggested by Dr. Hulett. Transportation and rough treatment have not caused the contents of the two compartments of these cells to mix in the slightest degree.

DOMINION ASTRONOMICAL OBSERVATORY,
OTTAWA, October, 1907.

A DEVICE FOR PREVENTING BUMPING IN THE MERCURY AIR-PUMP.

BY RALPH E. DELURY.

IN the use of the mercury air-pump one experiences the disagreeable "bumping" of the mercury, which sometimes results in the breaking of the pump. This may be avoided by using the device described below.

In Fig. 1 the ordinary form of air-pump is represented. The

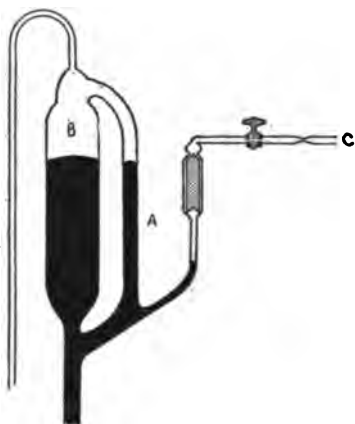


Fig. 1.

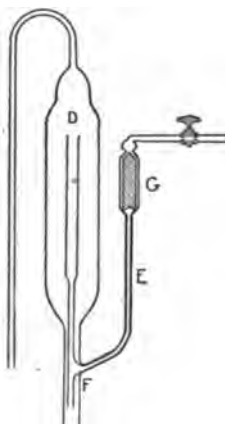


Fig. 2.

"bumping" is caused by the impact of the mercury which is shot up the side tube *A* with a velocity depending on the difference of pressure in the bulb *B* and the apparatus to be exhausted *C*. In a measure this may be stopped by not exhausting *B* so completely that there is a great difference of pressure in *B* and *C*. However the trouble is completely removed by replacing the side tube *A* by a tube inside the bulb, such as *D*, Fig. 2. The tube *E* is a thick-walled tube of about 2 mm. bore. It is sealed into the side of the vertical tube at *F* and inside *F* it makes a T-seal with *D*. The

tube *D* is open at both ends. The lower part of *D* should be about 4 mm. in diameter, and the upper part about twice this bore.

If now the mercury be caused to rise it will flow up through *D* and the bulb around it, and up into tube *E* until it closes the valve *G*. The air is forced out of the bulb and when the mercury flows back the pressure in *E* will cause the air to enter tube *D* before the mercury is all out of it. The mercury in *D* will thus be forced upwards as the air from *E* expands into the vacuum above, but since *D* is larger than *E* the mercury sprays very gently out of the end of *D*. Even if the mercury were shot up swiftly through *D* it would strike the solid curved top of the bulb without danger of breaking it or without causing the pump to vibrate transversely as is the case in the ordinary form.

A pump of this construction, used along with a water suction for lifting and lowering the mercury, has proved to be very satisfactory.

DOMINION ASTRONOMICAL OBSERVATORY,
OTTAWA, October, 1907.

PROCEEDINGS
OF THE
AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE THIRTY-EIGHTH MEETING.

THE Fall meeting of the Physical Society was held in Fayerweather Hall, Columbia University, New York City, on Saturday, October 19, 1907, President Edward L. Nichols presiding.

The following papers were presented:

1. Results of Careful Weighings of a Magnet in Various Magnetic Fields. L. A. BAUER.
2. On the Emissivity of Molten Iron and Copper. C. B. THWING.
3. The Selective Reflection characteristic of Salts of Carbonic and other Oxygen Acids. LEIGHTON B. MORSE.
4. The Variation of the Light Sensitiveness of the Selenium Cell with Pressure. F. C. BROWN and JOEL STEBBINS.
5. The Recovery of Selenium Cells after Exposure to Light. ERNEST MERRITT.
6. Wave-length—Luminosity Curves for Normal and Color-blind Eyes. F. L. TUFTS.
7. The Behavior of Selenium under the Action of Radium Rays, and some Recovery Curves for the Same. F. C. BROWN.
8. An Investigation of the Electric Displacement and Intensities Produced in Insulators by their Motion in a Magnetic Field, and its Bearing on the Question of the Relative Motion of *Æther* and Matter. (Read by title.) S. J. BARNETT.

It was announced that the usual Thanksgiving meeting in Chicago would be omitted, and that the Physical Society would meet in Chicago during Convocation Week in connection with the meeting of the American Association for the Advancement of Science.

Adjourned.

ERNEST MERRITT,
Secretary.

RESULTS OF CAREFUL WEIGHINGS OF A MAGNET IN VARIOUS MAGNETIC FIELDS.¹

BY L. A. BAUER.

A DISCUSSION of the results obtained by the magnetic survey yacht "Galilee" in the Pacific Ocean led the author to the tentative assumption, as announced at the meeting of the society last spring, that the earth's action on a magnet might not necessarily be everywhere that of a couple. Owing to the nonfulfillment, for one cause or another, of the conditions necessary to produce an exact couple there would be in addition a resultant force of translation. The cause may be a purely artificial one, due to some instrumental defect, *e. g.*, magnetic impurities in the metal used, or a natural one because of lack of uniformity in the magnetic field at the place of observation.

This hypothesis has been subjected by the writer during the past summer to a series of preliminary tests, involving careful weighings of a magnet, using a non-magnetic Becker analytical balance, embracing the region of the earth from Washington, D. C., to Sitka, Alaska.

The magnet was weighed in two horizontal positions (north end towards magnetic north and next reversed so that north end was towards magnetic south) and also in two vertical positions (north end up and north end down). The weighings were made at Sitka (Alaska), Victoria (British Columbia), Baldwin (Kansas), and Washington, D. C. At these places the earth's magnetic field is approximately uniform, *i. e.*, no marked local disturbances are known to exist.

The magnet was invariably weighed in both scale pans and the weighings in general were extended over two days at each station. In general the result for magnet, north end south, was greater than for north end north, the average difference being nearly $\frac{1}{100000}$ part of the weight of the magnet (about 33.6 grams). The differences in the weighings for the two vertical positions ($U - D$) were sometimes positive and sometimes negative, the average, regardless of sign, being of about the same order of magnitude as for the horizontal positions.

Weighings were also carried out in the intensely locally disturbed area at Treadwell Point, Douglas Is. (Alaska). Here the average difference for four points of observation was 0.07 mmg. (about $\frac{1}{800000}$ part) in the case of the two horizontal positions of magnet (weight for north end south being again greater) and for the two vertical positions, 0.25 mmg. or nearly $\frac{1}{100000}$ part (weight north end down being the greater). The

¹ Abstract of a paper presented at the New York meeting of the Physical Society, October 19, 1907.

differences are thus more pronounced — as was to be expected — than for the comparatively undisturbed fields.

Upon return to Washington, the investigation was amplified so as to embrace another magnet of different style, make and magnetic moment, and the weighings made for eight equidistant orientations of magnet (north end towards magnetic north, NE., E., etc.). Besides this, the balance itself was "swung" in order that the beam would not always be directed in the same way for the same orientation of magnet so as to exclude in every way possible any effect that might be attributed to magnetic impurities remaining in the balance, which the special tests failed to disclose. It was found that the orientation of *balance* had no appreciable effect upon the results obtained.

However, a systematic curve of differences or residuals from the mean weight, for the eight orientations of *magnet*, resulted — somewhat similar to the deviation curves which represent the effect on the compass of the iron on board a vessel. Two waves of about the same amplitude were clearly discernible — a semicircular one and a quadrantal one — the latter apparently associated with the inductive effect of the earth on the magnet in its various positions. On account of the presence of the quadrantal term, reversal of magnet does not eliminate the effect on the weight due to the outstanding residual magnetic force of translation. Hence the mean result of weighings of a magnet in two positions 180° apart will not necessarily give the true weight, or say the weight which the same substance would have if demagnetized. This was proved also by repeated magnetizations and demagnetizations of two different magnets. To get the true weight of a magnet within the accuracy attainable with the balance used, the weighings of the substance when magnetized would have to be made for *at least* eight equidistant positions.

The observations were repeated on three days, October 10, 11 and 12, at the Coast and Geodetic Survey Magnetic Observatory at Cheltenham, Md., and practically the same results obtained as before.

For the two stations, Washington and Cheltenham, the range in the results for the various orientations of magnet was about 0.05 mmg. ($\frac{1}{88000}$ part of weight of magnet).

The investigation is being continued.

THE SELECTIVE REFLECTION CHARACTERISTIC OF SALTS OF CARBONIC AND OTHER OXYGEN ACIDS.¹

BY LEIGHTON B. MORSE.

I. *The Selective Reflection of Carbonates as a Function of the Atomic Weight of the Base.*

POLISHED plane surfaces of (Mg, Ca, Fe, Mn, Zn, Sr, Ba and Pb) CO₃ were prepared and the ratio of the reflected to the incident radiation was measured at short wave-length intervals between 4 μ and 15 μ . The following are the principal conclusions reached:

1. The reflection curves for all the carbonates examined show between 4 μ and 15 μ three and only three bands of abnormal reflection. Abnormal reflection interpreted means a free resonance period of the molecule.

2. The bands fall into three separate and definite spectral regions, which are distinct from the regions where the salts of other acids, so far as known, show reflection maxima.

3. With few exceptions, an increase in the atomic weight of the base causes a shift of all three reflection maxima toward long waves of an amount roughly proportional to the change in atomic weight of the base. This is shown for the first reflection band by curve *a*, Fig. 1, in which the atomic weights of the bases are plotted as ordinates and the wave-lengths of the first reflection maxima as abscissæ.

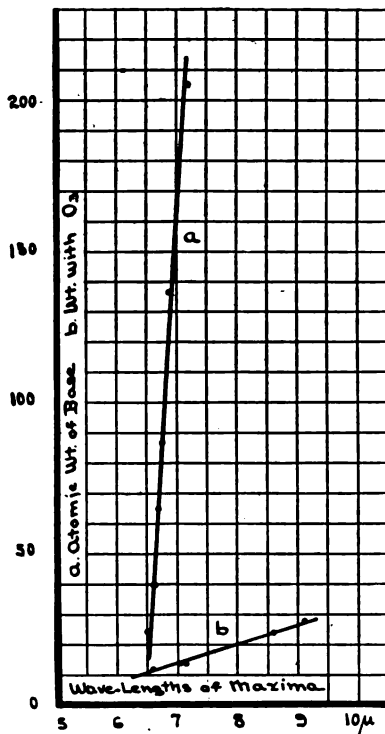


Fig. 1.

II. *The Rôle Played by Oxygen in the Selective Reflection of Carbonates, Nitrates, Sulphates and Silicates.*

Combining with the data on carbonates the scattered observations of other observers on nitrates, sulphates and silicates, the tentative hypothesis has been made that the

¹ Abstract of a paper presented at the New York meeting of the Physical Society, October 19, 1907.

oxygen atom is the one chiefly responsible for the marked reflection observed.

The wave-lengths of the first reflection bands in CaCO_3 , KNO_3 ,¹ CaSO_4 , and MgSiO_3 ,² are plotted as abscissæ, curve *b*, Fig. 1, and as ordinates, the weights of the acid-forming elements combined with O_2 , ($\text{C} = 12$; $\text{N} = 14$; $\frac{3}{2}\text{S} = 24$, and $\text{Si} = 28$).

The lines drawn show clearly that a small increase in the weight of the acid-forming element produces a much greater displacement of the reflection band than does the same increase in the weight of the base; and this is in full agreement with the chemists' view of the relative strength of the bond existing between the *acid-forming element* and oxygen and that between the *base* and oxygen.

The results suggests a new and far-reaching method by which it may sometimes be possible to express the dynamical relations existing between the separate atoms of a molecule, and thus the present conception of chemical bonds and linkages be given a broader significance.

The paper appears in full in the *Astrophysical Journal* for November, 1907.

THE VARIATION OF THE LIGHT SENSITIVENESS OF THE SELENIUM CELL WITH PRESSURE.³

BY F. C. BROWN AND JOEL STEBBINS.

THIS investigation is a continuation of the work reported to the American Physical Society at its February meeting in 1905, when it was shown for pressures from 0 to 600 atmospheres that the change of resistance of the selenium cell was approximately a linear function of the pressure.

It deals chiefly with the results of observations of the light effect at different pressures and states the results of a comparison of the light effect at different pressures with the light effect at different temperatures.

The following is a summary of the observations taken with a Giltay cell of which .3 sq. cm. of the surface was illuminated by a one c.p. incandescent light at 30 cm. distance. Each series is obtained from the average of fifteen exposures.

From these and other data the following conclusions were made:

1. The pressure effect is a genuine effect in the selenium itself and not a change in the contact resistance between the electrodes and the selenium or between parts of the selenium itself.

¹ Two values are plotted for KNO_3 corresponding to the results obtained by two independent observers, Pfund and Coblenz.

² If a correction be applied to correct for Mg being lighter than Ca this would bring the MgSiO_3 point even nearer the line drawn.

³ Abstract of paper read before the American Physical Society, October 19, 1907.

2. The light effect decreases with pressure when expressed in ohms or in percentage.

Series.	I.	II.	III.	IV.
Resistance of cell in ohms { pressure on	2,607,000	2,270,000	2,133,000	1,915,000
{ pressure off	2,850,000	2,878,000	2,435,000	2,530,000
Mean pressure in pounds	730	2,075	520	1,930
Change in resistance due to light { pressure on	185,000	131,000	149,000	164,000
{ pressure off	220,000	200,000	178,000	245,000
Percentage change of resist- ance due to light { pressure on	7.11	5.77	6.99	8.59
{ pressure off	7.70	6.92	7.32	9.70
Change of light effect due to pressure	0.59	1.15	0.33	1.11
Change of light effect per lb. pressure	.00083	.00056	.00065	.00058

3. The percentage decrease of resistance due to light is a function of the initial resistance, whether this initial resistance be conditioned by pressure or temperature.

THE RECOVERY OF SELENIUM CELLS AFTER EXPOSURE TO LIGHT.¹

BY ERNEST MERRITT.

IT has long been known that the increase in the conductivity of selenium that results from illumination is not an instantaneous effect. It is necessary to wait a considerable time after the exposure to light has begun before the final steady value of the resistance is reached. The recovery of selenium after illumination is even slower. In some cases the cell must be kept in the dark for several hours before the resistance comes back to its original value. While several observers have recorded observations which illustrate this gradual recovery, and which in some instances make it possible to plot a curve showing the relation between resistance and time, the subject does not appear to have attracted very great attention.

The writer has recently made observations on the recovery of selenium cells as influenced by the duration and intensity of the previous excitation, and finds a remarkable resemblance between the behavior of selenium, as indicated by the change in its conductivity, and the behavior of a phosphorescent substance, as indicated by the intensity of its phosphorescence. It was in fact the expectation that such a resemblance would obtain that led to these observations being made.

The cell used had a resistance in the dark of about 50,000 ohms. It was placed in a circuit containing a dead beat galvanometer and an E.M.F. of

¹ Abstract of a paper presented at the New York meeting of the Physical Society, October 19, 1907.

about 1 volt, and was excited by an acetylene flame at a distance of about 40 cm. The curves of Fig. 1 correspond to excitations of 10 seconds, 30 seconds and 300 seconds respectively. The method of plotting the curves is to take the difference between the observed conductivity C and the normal conductivity C_0 (measured in the dark), and to plot as ordinates the values of $(C - C_0)^{-1}$. This method of plotting was suggested by the results obtained by Nichols and Merritt for the decay of phosphor-

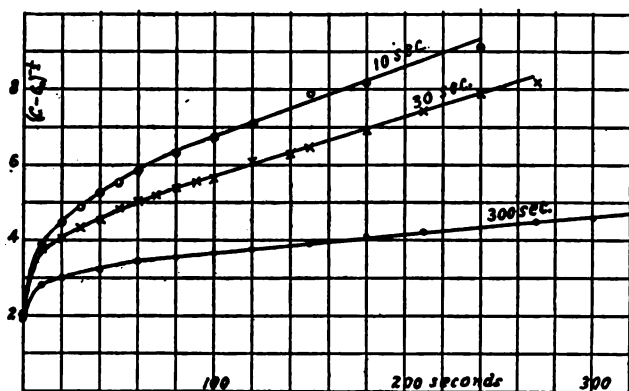


Fig. 1.

escence in Sidot blende,¹ where a linear relation between I^{-1} and t was found to hold after the first 40 seconds. The effect produced by light in Sidot blende is indicated by the intensity I of phosphorescence, while in selenium the effect of light is indicated by the increase in conductivity $C - C_0$. In order to facilitate a comparison of the behavior of selenium and Sidot blende a group of decay curves for the latter substance is shown in Fig. 2, this figure being reproduced from the article just referred to. In the curves of Fig. 2 the excitation was varied from 1.2 seconds in curve A to 900 seconds in curve F .

The resemblance between the two groups of curves is so striking as to suggest some real similarity between the two processes. In each case the curves start out concave toward the axis of t , but soon change into lines that are so nearly straight that the deviation is less than the experimental errors. The effect of increasing the duration of excitation is in both cases to prolong the time required for recovery, *i. e.*, to make the straight part of the curve more nearly horizontal.

In the case of Sidot blende, Nichols and Merritt have found that the relation between I^{-1} and t is also linear during the first seven seconds of

¹ PHYSICAL REVIEW, Vol. XXIII., p. 37, 1906.

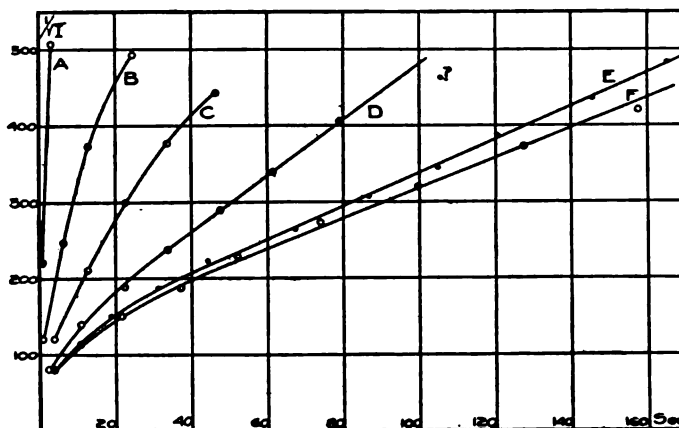


Fig. 2. Effect of duration of excitation upon the phosphorescence of Sidot blende. The times of excitation were as follows :

Curve A, 1.2 sec.

" B, 5.4 sec.

" C, 12.0 sec.

Curve D, 37 sec.

" E, 60 sec.

" F, 15 min.

decay,¹ so that the complete curve seems to consist of two straight portions connected by a region of rather sharp curvature. By the method thus far used with selenium I have not been able to make observations within the first 10 seconds. I find, however, that the recovery of selenium

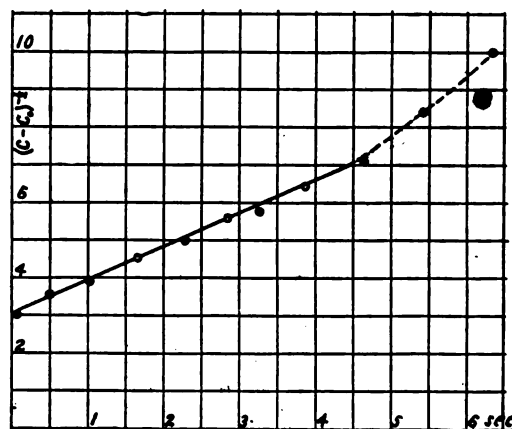


Fig. 3.

during the first few seconds after the end of excitation has been studied by Majorana² whose results, plotted in the manner explained above, are

¹ PHYSICAL REVIEW, Vol. XXII., p. 279, 1906.

² Rendiconti dei Lincei (5), 3, p. 183, 1894.

shown in Fig. 3. It will be noticed that the relation between $(C - C_0)^{-1}$ and t is linear for the first 5 seconds.¹ The behavior of selenium thus seems to be similar to that of Sidot blende in the earlier stages of recovery as well as later.

Another resemblance between the two phenomena is met with when we consider the effect of varying the intensity of excitation. In the case of Sidot blende a series of decay curves taken with constant time of excitation but increasing intensity is found to be somewhat similar to a series taken with constant intensity and increasing duration.² I have found that the same is true with selenium.

It seems not unlikely that the sharp curvature of the curves of Figs. 1 and 2 in the early stages of decay is due to the fact that the exciting rays penetrate only a short distance below the surface. The surface layer is in consequence excited far more strongly than the interior and decays with corresponding rapidity. After a short time the conditions will be more nearly uniform throughout and the decay will be more gradual. If experiments could be made with a sufficiently thin layer it seems not unlikely that the curves would be straight throughout their whole course.

If the increased conductivity of selenium produced by light is due to temporary dissociation, as has been suggested by Bidwell, it is of interest to note that the linear relation between $(C - C_0)^{-1}$ and t corresponds to a substance of the type CuCl_2 .

THE EFFECT OF RADIUM ON THE RESISTANCE OF THE SELENIUM CELL.³

By F. C. BROWN AND JOEL STEBBINS.

THE work in this paper was with a Ruhmer cell when exposed to radium of from 2 to 3 million activity. Two series of curves were shown showing the decrease of resistance with time of exposure, when the distance of the radium varied from .1 inch 4.1 inches. Another series of curves were shown showing the decrease of resistance with time of exposure when different thicknesses of mica were interposed between the radium and the selenium. And still another series of curves were shown showing the recovery of resistance with time. The amount of decrease of resistance varied from 30 to 0 per cent.

¹ The deviation of the last two points from the straight line does not possess great significance, since when $C - C_0$ is small the value of the corresponding ordinate will be greatly influenced by small errors in either C or C_0 .

² Nichols & Merritt, *PHYSICAL REVIEW*, Vol. XXII., p. 37, 1906.

³ Abstract of paper read before the American Physical Society, October 19, 1907.

From these curves it was shown that the decrease of resistance was due chiefly to the action of the β -rays. The variation of resistance change with distance was also deduced.

The rate of recovery from radium exposure was found to be about five times less than for light exposures of short duration.

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